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<b>(21) International Application Number:</b> PCT/GB91/00868 <b>(22) International Filing Date:</b> 31 May 1991 (31.05.91)  <b>(30) Priority data:</b> 9012315.9 1 June 1990 (01.06.90) GB  <b>(71) Applicant (for all designated States except US):</b> COURTAULDS COATINGS (HOLDINGS) LIMITED [GB/GB]; 18 Hanover Square, London W1A 1AD (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> SINCLAIR-DAY, John, David [GB/GB]; 13 Jasper Avenue, Greenside, Ryton, Tyne & Wear NE40 4RS (GB). CASSIDY, Stephen, Paul [GB/GB]; 8 Birtley Close, Kingsmere, Gosforth, Newcastle upon Tyne NE3 4RL (GB). RING, John [GB/GB]; 26 Meadowvale, Darras Hall, Ponteland, Newcastle upon Tyne NE20 9NF (GB). CORDINER, Andrew, George [GB/GB]; 90 Benton Road, High Heaton, Newcastle upon Tyne NE7 7DX (GB).	<b>(74) Agents:</b> SENIOR, Janet et al.; Abel & Imray, Northumberland House, 303-306 High Holborn, London WC1V 7LH (GB).  <b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, PL, SE (European patent), SU, US.  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> POWDER COATING COMPOSITIONS  <b>(57) Abstract</b>  A composition of the present invention for application as a powder coating is in the form of a fused agglomerate of different particulate components consisting of a primary film-forming component and one or more other components selected from film-forming and non-film-forming components. The agglomerated composition may be used to introduce a variety of additives into powder coatings and to provide a variety of aesthetic effects, both in single-layer and multilayer systems.		

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Powder Coating Compositions

This invention relates to powder coatings.

Powder coatings generally comprise a solid film-forming resin, usually with one or more pigments. They can be thermoplastic but are more usually thermosetting, incorporating two co-reactive film-forming resins or incorporating a curing agent for the film-forming resin in the powder particles.

10 Powder coatings are generally prepared by intimately mixing the ingredients, for example in an extruder at a temperature above the softening point of the film-forming resin but below the curing temperature of the composition (the process of extrusion), and comminuting the mixture  
15 to the desired particle size in suitable grinding equipment (the process of micronising).

The powder may be applied to the substrate by various means, for example by the use of fluid beds, or most commonly by electrostatic spray gun, and ideally the  
20 particle size distribution required for most commercial electrostatic spray apparatus is between 10 and 120 $\mu$ m, with a mean particle size by volume within the range of 15-75 $\mu$ m. (All mean particle sizes quoted herein are by volume.) Generally, the powders have at least 90% by  
25 volume of particles between 20 $\mu$ m and 100 $\mu$ m and no more than 70% < 50 $\mu$ m, and have a mean particle size at least

35 $\mu$ m, and generally no more than 60 $\mu$ m, often in the range of from 35 to 55 $\mu$ m, usually 35 to 50 $\mu$ m. In the electrostatic spray process the powder coating particles are electrostatically charged and the charged particles are attracted to the substrate which is earthed or oppositely charged. The powder coating which does not adhere to the substrate can be recovered for re-use, so that powder coatings are economical in use of ingredients as well as non-polluting to the environment. The powder is then cured on the substrate by the application of heat (the process of stoving) usually for a period of from 5 to 30 minutes and usually at a temperature in the range of from 150 to 220°C, although temperatures down to 120°C may be used for some resins, especially epoxy resins; the powder particles melt and flow and a film is formed.

Various different finishes, for example reduced gloss and textured finishes, may be obtained.

Reduction of gloss in the powder coating from full gloss (80-90% measured at a 60° viewing angle) to some other lower level, for example satin gloss (55-65% gloss) or matt (< 30% gloss), is achieved by creating a surface which is rough on a microscopic scale. This surface roughness must be sufficient to cause a reduction in the specular reflection from the film by scattering the incident light; if it is visible, however, a texturing effect is achieved in the film. In liquid paints this gloss reduction is usually achieved by the use of pigment

and/or filler particles at high volume concentrations. However, this technique cannot be used as the sole route to gloss reduction in powder coatings as a high content of filler particles would lead to too reduced a surface  
5 flow during curing.

The procedure used is to set up reactions within the curing film such that two different gelation rates are set up within the curing matrix. With acid-functional polyesters, a fast gelling (reacting) powder and a slow  
10 gelling powder may be manufactured separately and mixed after the micronising stage or, more usually, the components are mixed prior to micronising. The faster gelling domains form particles which disrupt the surface flow of the slower gelling portion of the matrix. For  
15 production simplicity and economics, a one-component matt is preferred, but the production of an adequate range of matt finishes using a one-component system is not possible in all resin types, and there is no single matting agent that can be used with all resin types to  
20 provide a wide variation of gloss levels.

For texture, there are a wide number of agents that can be added to powders to achieve different surface effects, acting by disrupting the flow of the polymer film. For a stippled finish, micronised PTFE (polytetra-  
25 fluoroethylene) is used. For a wrinkle finish, cellulose acetate butyrate resin (CAB) or acrylate homo- and copolymers may be used; an example of the latter is

Acronal 4F (Trade Mark), which is usually added before extrusion as a flow aid, but which in micronised form is used for texturing. For a hammer finish (gross surface depressions), a metallic pigment and texturing agent are  
5 used. In addition, texturing agents based on high molecular weight thermoplastics are commonly added to thermoset powder coatings, giving rise to uniformly poor flow across the surface which manifests itself as a texture.

- 10 PTFE is preferably added to the premix before extrusion and is fully incorporated into the extrudate in order to minimise product variation through segregation. However, the micronised PTFE has to be prepared in a particular fashion to give batch-to-batch consistency.
- 15 CAB may be added to the finished powder or, since as a post-additive it is prone to segregation with use, preferably at the premix stage. It does not melt in the extruder, and the inhomogeneous dispersion thereby produced gives rise to the texture. Some texturing  
20 agents, however, for example Acronal 4F (T.M.), have to be added post-extrusion since the extrusion process would render them ineffective by mixing them intimately with the continuous phase of the coating system. Powders containing post-additives are susceptible to segregation  
25 which causes inconsistency in the texturing effect on application of the powder.

Multilayer coatings may be produced using mixed

polymer systems by stratification or "surface segregation" of incompatible phases during film formation. Mixtures of, for example, an acrylic polymer and polyester may be used to form a multilayer coating, with  
5 the acrylic polymer migrating to the surface of the coating (the air interface) and the polyester forming the lower layer on the substrate. As compared with pure polyesters, the multilayer coating provides improved stain, solvent and UV resistance, for example resistance  
10 to degradation by sunlight, and improved durability and weathering performance, and, as compared with pure acrylic, improved mechanical performance.

If powders are made by pre-mixing both the polymers prior to extruding, however, the stratification is not  
15 uniform from formulation to formulation or from colour to colour, such that the improvements described cannot be guaranteed. If, alternatively, acrylic and polyester powder coating powders are mixed prior to application, stratification can be complicated by the formation of  
20 textured films due to the incompatibility of the two polymer systems. The two powders will also be subject to problems of segregation of the powders in the solid state.

Our copending application GB 2226824 A describes a  
25 colour mixing process for powder coatings in which sufficiently small-sized particles,  $< 20\mu\text{m}$  in size and advantageously  $< 10\mu\text{m}$ , are used that mixed colours

applied to a substrate have homogeneous appearance.

Before application to the substrate the mixture is generally subjected to a process of agglomeration in which the small-sized particles are fused into composite  
5 particles, for example by mechanofusion, for example at a temperature in the range of from 60 to 80°C, and this converts the mixture from a cohesive mass to a free-flowing and fluidisable powder, which can be applied by conventional means. Agglomeration also prevents segregation  
10 tion of the constituents during application and handling, which is otherwise bound to occur, for example during the application process itself (because of differential electrostatic charging) or in the attendant recovery and recycling process (because of differences in particle  
15 size and/or particle density) or in transport, causing batch-to-batch variability in the resulting coating.

The present invention is based on the realisation that formation of a fused or bonded agglomerate provides a suitable method, not only for colour mixing, but also  
20 for the introduction of a variety of additives into powder coating compositions, both in single layer and multilayer systems.

The agglomeration process has had a number of advantages:

25 (i) Firstly, the agglomeration process provides an extension of our colour mixing process to give a range of aesthetic effects.



(ii) Secondly, it provides effectively a permanent fixing in the composition for known materials which would be prone to segregation in the solid state during the handling process, for example in transportation and application, and during recycling of over-sprayed particles.

Thus, more especially, it has led to the production of gloss-reduced and textured coatings which do not have the disadvantages described above of conventional such coatings.

(iii) Thirdly, with mixed polymer systems it facilitates enhancement or manipulation of segregation (stratification) within the film during film formation.

Thus, it has led to the production of more satisfactory multilayer coatings that do not have the above-mentioned disadvantages of the prior art systems.

(iv) Fourthly, incorporation of additives by agglomeration, rather than extrusion, provides the potential for the preparation of a variety of new products which could not be manufactured by conventional routes (e.g. extrusion and micronising), for example because the additive would be damaged by the manufacturing process, or would be likely itself to damage the process equipment.

25 Metallic pigments such as, for example, aluminium or 'gold bronze' flakes are used in powder coating to add lustre to the coating finish; the most common metallic

pigment used is aluminium. In a "leafing" system, the aluminium flakes orient themselves in a continuous layer at or near the surface of the film, producing an opaque silver finish. The pigments are usually incorporated by dry blending; a lustre effect, achieved by the pigment "leafing", for example, may easily be destroyed by strong shear forces, such as those found in extruders and micronisers. However, the loose metallic flakes can cause unwanted electrical discharge within the spray gun, and the presence of free metallic pigments within the powder(s) also represents a significant increase in explosion hazard.

These problems have been overcome by a special technique developed by Wolstenholme Bronze Powders Ltd.. The technique involves a mechanofusion or bonding of the individual flakes of metallic pigment to the surface of conventional powder coating particles; as soon as the powder begins to melt during stoving the metallic flakes are released and rise to the surface with the powder coating film, thereby producing a good leafing effect and a bright metallic finish. A range of hammer and other textured metallic finishes can be produced by using, in addition, an appropriate hammer or structure additive. In the review "Ten Years of Bonded Metallic Powder Coatings" by Keith S. Carter in Polymers Paint Colour Journal, Volume 176, No. 4179, November 1986, the author indicates that, although the bonding process is used

mainly with flaky metallic pigments, other pigments such as pearlescent pigments - which, like metallic pigments, should not be extruded and ground, and which give a special finish -can also be successfully bonded.

- 5 However, the technique has not previously been applied beyond the specific field of metallic or lustre finishes, and nor have there been any suggestions to do so.

Accordingly, the present invention provides a composition suitable for application as a powder coating  
10 and which is in the form of a fused agglomerate of different particulate components, with the exception of the agglomerated composition claimed in GB 2226824 A and of the bonded metallic powder coatings described above.

A number of powder coating processes using combina-  
15 tions of separate components have been proposed, generally with the aim of reducing blocking (clumping) in the powder on storage.

US Patent 4,260,066 (Celanese Corporation) describes powder coatings in which small tacky particles comprising  
20 a melt flow modifier and adhesion promoter are adhered to non-tacky particles containing a thermoplastic elastomer, melt flow modifier, adhesion promoter and stabiliser, to form composite particles which do not agglomerate on storage.

25 Pending applications EP 0 250 183 A, EP 0 372 958 A and EP 0 389 080 A (Nippon Paint Company Limited) describe the addition of, respectively, cross-linked

polymer particles (usually microparticles), an anisotropic crystalline polymer (usually in the form of microparticles), and microparticles of comparatively high Tg to a base resin at any stage of preparation. The components may, for example, be combined during the mixing, milling, pulverising or sieving steps or, in a wet process, may be dispersed together in an appropriate solvent or may be combined in the subsequent spray-drying step.

However, in none of the Nippon Paint or Celanese Corporation processes described is the second component firmly fixed to the surface of the first component and resistant to separation by mechanical or electrostatic forces.

More especially, the present invention provides a composition suitable for application as a powder coating and which is in the form of a fused agglomerate of different particulate components, provided that,

- if the agglomerate contains a metallic or lustre component and a film-forming component of mean particle size 35 to 60 $\mu$ m and no more than 70% by volume < 50 $\mu$ m, it also contains an incompatible film-forming component or a non-film-forming performance component or two or more such components, and
- if the agglomerate contains two or more differently coloured compatible film-forming components and optionally an uncoloured compatible film-forming

component and the size of the particles in each of those film-forming components is sufficiently low that when the powder coating is applied to a substrate and heated to form a continuous coating the differences in colour in the cured powder coating arising from the different coloured and any uncoloured particles cannot be discerned by the human eye, it also contains an incompatible film-forming component or a non-film-forming component or two or more such components.

More especially, the present invention provides a composition suitable for application as a powder coating and which is in the form of a fused agglomerate of different particulate components, provided that,

- 15    - if the agglomerate contains a metallic or lustre component and a fluidisable film-forming component, it also contains an incompatible film-forming component or a non-film-forming performance component or two or more such components, and
- 20    - if the agglomerate contains two or more differently coloured compatible film-forming components and optionally an uncoloured compatible film-forming component and the size of the particles in each of those film-forming components is sufficiently low
- 25    that when the powder coating is applied to a substrate and heated to form a continuous coating the differences in colour in the cured powder

coating arising from the different coloured and any uncoloured particles cannot be discerned by the human eye, it also contains an incompatible film-forming component or a non-film-forming component or two or more such components.

An agglomerate of the present invention contains one or more film-forming systems (polymeric binder systems) and usually contains also at least one colouring agent. A film-forming system itself comprises a solid film-forming resin and any curing agent required therefor. (By a film-forming resin/polymer we mean one that acts as a binder, that is, that has the capability of wetting pigments and providing cohesive strength between pigment particles and that wets or binds to the substrate, and that melts and flows in the curing/stoving process after application to the substrate to form a homogeneous film.) Usually any colouring agent or agents (pigments and/or dyes) and any curing agent is extruded with the or with one or more of the film-forming resins so that particles formed therefrom comprise a film-forming resin and colouring agent or agents and/or curing agent; generally at least the majority of such particles contain at least one colouring agent. However, any colouring agent and any curing agent may each, if desired, be present as a separate component. There may, if desired, be two or more film-forming components in the agglomerate; each may be coloured or uncoloured.

One or more other additives may, if desired, be contained in the agglomerate; each may be in a film-forming component or as a separate component (a non-film-forming component).

- 5       A non-film-forming additive, which may, if desired, be present as a separate component, may be one having an effect on performance (a "performance additive" or "functional additive"), and/or an aesthetic effect (an "aesthetics additive"), usually a visual effect (an
- 10 "appearance additive"). A performance additive may be one bringing about an effect on the resulting coating and/or on the application process or the curing process.

- Any two or more components in the agglomerate may be compatible or incompatible with each other. For example,
- 15 the agglomerate may comprise two compatible film-forming components, for example of different colour, or one coloured film-forming component and one uncoloured (compatible) film-forming component (used, for example, to provide additional resin content to improve flow); or
- 20 two incompatible film-forming components, for example of the same colour or one coloured and one uncoloured, and, if desired, a further component which may be compatible with one of the other two components. (For example, the three-component system acrylic, epoxy and polyvinylidene
- 25 difluoride (PVDF) comprises two phases, the PVDF being "compatible" with the acrylic but not the epoxy.)

If desired, one or more of the film-forming

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components may contain a non-film-forming additive co-extruded with the film-forming agent. A separate, non-film-forming component may be compatible or incompatible with a film-forming component.

5       As will be explained in more detail below, the presence of incompatible components or components that generate incompatibility (both film-forming and non-film-forming) may be used to produce gloss reduction and/or texture in the powder coating: they are acting as  
10 aesthetics additives.

The incompatibility during film formation can be achieved, for example, by the use of polymers of different chemistry that are immiscible during agglomeration and during curing. For example, an acrylic component and a polyester, epoxy, polyester-epoxy or  
15 polyurethane component are incompatible, and cannot be blended to form a single (stable) phase. Such systems have such different surface tensions that gross defects are caused when one powder "contaminates" the other.

20       Incompatibility during film formation can also be achieved by using components that are initially miscible (compatible) but that become immiscible during curing. Thus, for example, two systems of similar chemistry and approximately the same gel time are compatible, but  
25 components with different gel times are initially compatible but become incompatible as curing (and molecular weight build-up) proceeds.



Materials that are incompatible during film-formation can separate into different phase domains which can give rise to incompatibility effects such as matting.

Aside from this, the presence of two materials of

5 different surface tension at the surface of the film and in discrete areas/domains can lead to surface disruption (texturing).

Alternatively, incompatible film-forming components, with different surface tensions, may be used to provide  
10 multilayer coatings: in this instance they are acting as performance additives.

**Aesthetics additives:**

Additives having an aesthetic effect include, for example, gloss-reducing additives, texturing agents, and  
15 additives to produce lustrous finishes (e.g. metallic and coated mica pigments). Advantageously, these are present as separate components.

**A. Gloss-reducing additives:**

We have found that a number of additives may be used  
20 as separate components in agglomerates of the present invention to reduce gloss.

1. An incompatible film-former; the component may be coloured or uncoloured.
2. A non-film-forming (or non-flowing) polymer, for  
25 example PTFE or a cross-linked or high-melting film-former, for example a high melting acrylic such as polymethylmethacrylate (which melts above 200°C);

these are insoluble in the film at the time of film-formation. They may be coloured or uncoloured.

3. Conventional gloss-reducing agents, that is those used for gloss reduction in conventional powder coatings, or extensions of such systems. In general, we believe they act by generating incompatibility in the curing reaction and/or by setting up a differential curing reaction when the coating film is formed. Examples are as follows:

- (a) A second catalyst which will give a much faster gel time than the principal catalyst used to cure the film; examples are the Ciba-Geigy products "XG 125" (zinc N-ethyl-N-phenyl dithiocarbamate) and "XB 3329" (the zinc salt plus a matting wax) that further reduces the gloss level, possibly through incompatibility.
- (b) For pure epoxy and epoxy-polyester (hybrid) systems, a catalyst which has a chemical structure that causes two rates of gelation on curing; examples are given in GB 1,545,780 and include the Hüls products B55 and B68 which are adducts of pyromellitic acid and 2-phenylimidazoline.
- (c) For polyurethane systems using hydroxy-functional polyesters cured with an isocyanate (typically isopherone diisocyanate), a hydroxy-functional polyester with a radically different

functionality (e.g. a hydroxy-functional polyester with a functionality of 7 added to one with a functionality of 2).

- 5 (d) A small proportion of an initially compatible film-former having a different gel time from that of the main film-former; for example for acid functional polyesters designed to cure with triglyceryl isocyanurate, a polyester of approximately the same colour, or uncoloured, 10 but with a different gel time.

4. Inorganic fillers of large particle size, usually up to 30 $\mu$ m in size.

We have found that clear "incompatible" particles of mean particle size < 5 $\mu$ m fused in an agglomerate with 15 a conventional powder component or with a film-forming component of smaller particle size, for example of similar particle size to that of the incompatible component, are very effective in producing reduced-gloss systems of very specific and unusual character (very low 20 loss, good flow and levelling, and good flexibility).

Thus, for example, when an acrylic component of small particle size is used as the minor component (up to 20% by weight) with a polyester component 90% by volume of particle size < 20 $\mu$ m in a fused agglomerate, matt 25 coatings caused by micro film defects, with very low gloss levels, may be obtained. Typically, gloss in a polyester system can be reduced to about 5% by addition

of 12% by weight of acrylic component. This second component may be uncoloured or, for example, the same colour as the first component. The system can be further manipulated according to polymer choice, gel time, particle size and filler level of the acrylic. Co-extrusion of such mixtures of materials would give full-gloss films with a degree of stratification of polyester/acrylic through the film. In contrast, using the dry blends of such materials (non-fused) at particle sizes acceptable for electrostatic application gives macro film defects, with some stratification giving rise to a higher than expected (relative to weights added) level of acrylic at the surface. The agglomerated material, however, does not suffer from particle segregation in the solid state as will dry-blended product, thus giving uniformity of product even after transportation and spraying, and the non-spangle matt finishes available using this technique have superior mechanical properties to polyester matt coatings produced by conventional techniques. Such an 'effect' is useful for example on non-reflective ceiling applications.

It should, however, be mentioned that when the acrylic component is added in very small proportions (e.g. 1%) and well mixed, the effects of incompatibility may not be evident. Similarly, with film-forming components of different gel time and of small particle size, the particles are intimately mixed and

incompatibility is at such a small scale that incompatibility effects are not noticeable.

We have also found that PTFE is an effective gloss reducer in fused agglomerates. For example, additions of  
5 as little as 10% by weight give films with gloss at 15% (60° gloss). This effect is believed to be highly dependent on the particle size of the additive. However, the cured films mar easily; for example the film can be polished by rubbing with a fingernail, cloth, etc.. We  
10 attribute the effect to removal of PTFE at the surface because the additive binds very poorly to the polyester: it is a hard, non-sticky material which does not soften at film-forming temperatures.

Heterogeneous catalysts such as XG 125 and B 55  
15 mentioned above are already used in powder coatings to provide novel effects, for example as matting agents. The catalyst would normally be applied to the milled powder by special techniques, but the agglomeration process of the present invention allows the introduction  
20 of a catalyst in a heterogeneous manner.

B. Texturing agents

Conventional texturing agents may be used in agglomerates of the invention, but preferably in a novel way, as separate components in the agglomerate. These  
25 include

1. the non-film-forming polymer PTFE,
2. CAB or other suitable film-forming polymer.

By the agglomeration bonding technique of the present invention, the problems encountered in the prior art with the use of texturing agents are avoided.

Thus, agents used as separate components in fused  
5 agglomerates may be able to act as matting and/or texturising agents, depending inter alia on the size of the component. Thus, for example, when the size of the PTFE particles in a gloss-reduced composition is increased and the amount of the PTFE component is  
10 decreased, a textured finish is produced.

We have found that textured films containing PTFE are less easily marred than gloss-reduced PTFE-containing systems, possibly because there is more free resin to bind each PTFE particle because there is generally less  
15 PTFE present, and the texturing PTFE is at a larger size and requires less binding resin.

A modification of the prior art use of high molecular weight thermoplastic added to a thermosetting system is the use of  
20 3. a high molecular weight film-forming polymer having a softening point lower than extrusion temperature (90 to 150°C), but higher than agglomeration temperature (preferably 60 to 80°C).

C. Metallic pigments:

Aluminium and a number of other metals and alloys e.g. stainless steel, copper, tin, bronze and brass (gold is generally too expensive), may be used to produce what are referred to as 'lustre' or 'glamour' finishes. The aluminium pigments are the most widely used today. Leafing systems have already been discussed. Non-leafing aluminium pigments, which orient themselves throughout the coating film, provide aesthetics quite unlike leafing aluminium pigments. They are unique in their ability to project 'flop', polychromatic, and sparkle effects. ('Flop' is the ability to change colour when viewed at different angles. This capability is directly related to flake orientation in the film.)

Mica pigments may also be used; these are thin platelets of the natural mineral mica coated with titanium dioxide and/or iron(III)oxide. The literature claims that the characteristic properties of their flat structure, high refractive index and transparency create effects in transparent media which, due to the multiple reflection of light, match the lustre of pearls or of mother-of-pearl.

Performance additives:

Various performance additives, the majority of these being non-film-forming components, include a number that could not be added in conventional powder coating manufacture. By allowing for the possibility of

incorporating additives post-extrusion, the agglomeration bonding process according to the invention leads in many cases to new products. Examples are:

A. Fragile additives:

5        1. Toughening agents:

Rubber toughening agents are used in the field of composites to prevent crack propagation. In order to be effective they need to have a well-defined size and shape. Extruding or micronising a  
10       sample might destroy its morphology and therefore its intrinsic properties, so that in order to maintain the morphology of the rubber toughener it would preferably need to be incorporated by a method other than extrusion. The agglomeration bonding  
15       technique of the present invention offers a method of incorporation of rubber tougheners without affecting their morphology. An example is the addition of rubber-like tougheners into acrylic resin systems which are highly durable but mechan-  
20       ically weak.

2. Friction-reducing additives:

Low-friction coatings frequently use polytetrafluoroethylene (PTFE) or nylon spheres. Addition of these type of materials by the agglomeration bonding  
25       method allows the materials to be used without risk of damage to their morphology, thus leading to the production of low-friction coatings, not producible



by any normal method of powder coating manufacture.

3. Strengthening agents:

5       Fibres, for example, confer structural strength to composite materials but would not survive extrusion; fibres may also be used to improve conductivity.

4. Microcapsules:

10       Microcapsules carrying a variety of pay loads can be added to liquid paints to bring about different effects. Many work because application of pressure or stress releases the active ingredient. Those used in the liquid paints that may now be used in the powder coating field, as separate components in a fused agglomerate, include

- 15       - bruisable microcapsules containing perfume,  
      - bruisable microcapsules containing aggressive solvents, for self-stripping coatings,  
      - bruisable microcapsules containing ink, dye or chemical precursor of either, for printing and  
20       other marking.

There are also some attractive new ideas in this area. For example, the use of

- microcapsules containing air, to improve opacity and perhaps cheapen the coatings,  
25       - microcapsules carrying plasticizer, to aid flow and levelling (and not necessarily only during stoving, perhaps also after impact of the cured

film, thus providing a self-healing coating);

- microcapsules containing zinc metal, to obtain anticorrosive coatings without the hazards of handling free metal powder;

5       - bruisable microcapsules containing pressure-sensitive adhesives, for example in post-formable coatings stress-induced release of adhesive may improve adhesion at areas of high deformation.

10    B.   Materials which may damage or lead to blockage of the extruder:

1.   Abrasive materials:

15       A non-slip powder coating incorporating sand as the non-slip medium may have a significant market for such things as ladders, gangways, etc..

Other abrasive materials, for example metal carbides, bauxite and certain other solid inorganic material/pigments, may also be used to provide, for example, non-slip coatings, sandpaper or abrasion-resistant coatings. For example, we have found that by including bauxite in a powder formulation, a coating offering substantial abrasive resistance is produced.

20       As these materials are hard (bauxite extremely so: 25       9 on Mohs scale) such coatings could not be produced by the conventional method due to the excessive wear which would occur to the internals of extruders.

The agglomeration process of the present invention enables this problem to be overcome, leading to the development of a new range of coatings.

In addition, the agglomeration bonding process of  
5 the present invention can be used to reduce extruder wear that occurs in conventional powder coatings with the use of certain fillers or extenders such as Syenex extenders. Fillers and/or extenders may be used not only, at large particle size, to reduce gloss (see above), but also as a  
10 partial replacement for resin, to reduce costs.

## 2. Catalysts:

Catalyst: Highly reactive catalysts and/or high levels of catalysts are desired to achieve either fast cure at the most common stoving temperatures  
15 (for example 170-220°C) or cure at lower temperatures. However, they would also cause significant cure at extrusion temperatures (usually 90-140°C), that is, the composition would have a short gel time even during extrusion, and this could lead to  
20 formation of "bits" in the final coating or even blockage of the extruder. The agglomeration bonding method of powder production according to the invention avoids the need for extrusion of the catalyst and offers a method of incorporating more  
25 reactive catalyst and/or higher than normal levels of catalyst.

C. Heat-sensitive materials:

Highly reactive curing agents/catalysts may be used to create ultra-low-bake coatings (baking at little more than extrusion temperature). This allows very heat-

5 sensitive materials, for example

- biological materials (e.g. fungicides or enzymes),
- intumescent pigments and
- thermochromic pigments,

to be included by agglomeration. Intumescent-type  
10 pigments foam and yield volatiles when heated and may be used for fire-resistance; such materials in fused agglomerates of the present invention may be included to yield heat- or sound-insulating coatings. Thermochromic pigments are also changed by heat, and are used, for  
15 example, on the outside of furnaces to monitor hot spots. Such products may also be used in fused agglomerates of the present invention to provide new and useful coating compositions.

Structuring of products:

20 In some instances it is desirable to structure the product in a particular way. This can provide advantages in terms of storage and application of the product.

D. Tribocharging and corona-charging additives:

Tribocharging additives are commonly present as free  
25 entities in the product, and it is important that they are able to contact the charging surface in the application gun. However, they are known to segregate, causing

problems on application. Introduction of this additive in the last stages of agglomeration may fix them to the surface of the product particle. Corona-charging additives might be used more effectively in a similar way.

5 E. Surface segregation:

Manufacture of the agglomerate in a controlled way also gives us a unique opportunity to control structure in the coating. Our observations suggest that stratification of incompatible phases during film  
10 formation is strongly dependent on the initial particle size of the discrete phases.

1. High exterior-durability systems;

Agglomeration of, for example, mixed reduced-size acrylic and polyester powders not only avoids  
15 problems of segregation, in the solid state, which is otherwise bound to occur, but also has been found to enhance stratification of the non-compatible phases in the molten state (with respect to 'extruder assembled' particles). This control of  
20 film structure offers enormous scope for new and improved products.

Effective multilayer systems containing the best properties of polyester and acrylic polymers have been sought after for some time. Although there is  
25 an underlying thermodynamic driving force to separate the two species so that the acrylic lies on the surface of the film, kinetic barriers and the

time constraint of film formation mean that this does not necessarily happen. We believe that use of an agglomerate of the present invention in which the two species start off as reduced-size discrete phases reduces the importance of kinetic barriers.

Other high exterior-durability systems can be devised. Particularly attractive ones use polyvinylidenedifluoride (PVDF). Its use is, however, limited by its poor adhesion to aluminium substrates and it may therefore be co-extruded with acrylic, then reduced in size and assembled in an agglomerate with reduced-sized epoxy, polyester, polyester/epoxy hybrid or polyurethane particles. Stratification of the PVDF/acrylic component over one of these chemistries at the interface provides a one-coat self-priming super-durable system. Alternatively, in some cases PVDF may also be used as film-forming component on its own, for example with epoxy as the other film-forming component; epoxy acts as an adhesion promoter.

## 2. Silicone non-stick substrates and anti-adhesives:

Silicone-type non-stick substances as used in antifouling coatings technology lack good bulk mechanical properties. Stratification of these film-forming components to yield a thin silicone surface film is advantageous for easy-clean domestic

appliances. Conversely, it may be desirable to achieve stratification of an 'anti-adhesive' to the underside to yield a peelable coating.

F. Porous coatings:

5 Powder coatings lack continuous porosity. It is inferred that because of this any effect which relies on transport through the film is denied. This includes the use of inhibitor pigments for anticorrosion, breathable coatings (e.g. for wood) or many forms of controlled-  
10 release. One way to increase porosity may be to increase pigment loading - as a separate component - well beyond critical pigment volume concentration. For example, traditional controlled-release  $\text{Cu}_2\text{O}$ -based antifoulings characteristically have pigment volume concentration  
15 >80%. Manufacture of powder coatings having very high PVC is not presently possible, but introduction of porosity may be enabled by the agglomeration process. A possibility is to use a soluble component, for example sodium chloride or other water-soluble inorganic product,  
20 at high levels. After formation of the powder coating the water-soluble product may be dissolved away, leaving pores.

We have found that the fusion agglomeration method of the present invention can bring about a dramatic  
25 increase in flexibility of the traditional powder manufacturing process and promote utilisation of plant. In our GB Application 2226824 A the concept has been

applied to the production of different colours, but now it is clear that other major parameters can be varied in a similar way. For example, gloss-controlling agents, texture agents and any of the above-mentioned other additives may be introduced at the mixing step for the two coloured components. In essence, formulation is moved further down the production line. The process of the present invention and GB Application 2226824 A also have the advantage of allowing a wide range of products of different appearance (colour, gloss, texture, etc.) to be obtained from a limited number of base colours. The possibility of adjusting pigment or resin content by adding pigment or uncoloured compatible film-forming particles as separate component also assists product flexibility.

#### Size of agglomerated particles

The size of the fused agglomerate particles is governed by the powder handling characteristics and powder application process and by the desired thickness of the resulting film.

Firstly, size must be consistent with appropriate bulk behaviour. Both particle size and, to a much lesser extent, density influence whether or not a powder is fluidisable, and in general powders having a mean particle size less than  $15\mu\text{m}$  are not readily fluidisable, in particular not by commercial electrostatic spray apparatus.



Generally, the agglomerated particles should be fluidisable. A method of measuring the flow properties of a coating powder is that developed at the Verfinstituut TNO (Metal Finishing Journal 1974); the equipment for this method is available as the 'Fluidimeter AS 100'. A standard quantity of powder, 250g, is placed in a vessel similar to a fluidised bed but which is fitted with a 4mm nozzle in the wall just above the porous plate. This nozzle is initially closed and air is passed through the vessel at a standard rate of 200 litres/hour. The powder is stirred during fluidisation until the height of the bed stabilises at a constant level,  $V_1$ , measured in cm. The air supply is switched off, the powder rapidly falls back to the 'at rest' level and the height is again measured,  $V_0$ . The air supply is then switched on again at the same rate as before and the powder allowed to reach a constant height. The nozzle is then opened for 30 seconds and the powder which runs out is collected and weighed in grams; at least five replicate measurements are made and the average (G) calculated. The flow factor, R, is defined by the formula:  $R = G \times \frac{V_1}{V_0}$ . It has been found empirically that this flow factor correlates very well with practical application properties.

<u>Flow factor, R</u>	<u>Free-flowing properties</u>
> 180	very good
140-180	good
120-140	acceptable
5 80-120	moderate
< 80	poor

Thus, for example, suitable agglomerated powders have flow factor  $\geq 80$ .

Generally, for a fused agglomerate, particle sizes  
10 no more than 1% by volume over  $120\mu\text{m}$ , for example up to  
 $110\mu\text{m}$ , preferably up to  $100\mu\text{m}$ , but preferably at least  
90% by volume more than  $5\mu\text{m}$ , especially at least  $10\mu\text{m}$ ,  
should be used. An agglomerate size of up to  $150\mu\text{m}$  may  
be appropriate for special purposes, for example for  
15 powder coating reinforcing bars in concrete. The mean  
agglomerate particle size (by volume) generally is no  
more than  $80\mu\text{m}$ , for example no more than  $75\mu\text{m}$ , preferably  
no more than  $60\mu\text{m}$ , for example no more than  $50\mu\text{m}$ , or no  
more than  $40\mu\text{m}$ , and generally at least  $15\mu\text{m}$ , for example  
20 at least  $20\mu\text{m}$ , preferably at least  $25\mu\text{m}$ . A mean in the  
range of from 10 to  $50\mu\text{m}$  should especially be mentioned.  
Thus, for example, an agglomerate particle size distribu-  
tion of 0- $120\mu\text{m}$ , preferably 5- $110\mu\text{m}$ , more especially 10-  
 $100\mu\text{m}$ , with a mean particle size (by volume) in the range  
25 of from 15- $80\mu\text{m}$ , preferably 20- $75\mu\text{m}$ , especially 25- $50\mu\text{m}$ ,  
may be used. (It should be noted that the particle sizes  
referred to herein are generally measured by light

scattering techniques.)

As to the thickness of the resulting film, for many current applications of powder coating technology, with thermosetting resins the film is approximately 50 $\mu$ m thick, but there are many current applications for powder coatings, and a plurality of film thicknesses are used. For decorative finishes, film thicknesses as low as 20 $\mu$ m are known, but it is more usual for the film thickness to fall within the range 25-120 $\mu$ m, with common ranges being 30-80 $\mu$ m for some applications, and 60-120 $\mu$ m or, more preferably, 60-100 $\mu$ m for other applications, while film thicknesses of 80-150 $\mu$ m are less common, but not rare. For functional coatings, similar ranges are found. However, there are some uses (for example, coatings for oil and gas pipe lines and for concrete reinforcing bars) where film thicknesses of 150-500 $\mu$ m are common and, for some encapsulation uses, film thickness can be measured in millimetres. In general, however, thinner coatings are cheaper and therefore preferred.

Thus, the size of the agglomerate should generally also be compatible with achieving the minimum suitable film thickness.

#### Size of component particles

The size of the individual components and the size of the agglomerate are clearly inter-related, and the choice of agglomerate and component particle sizes is influenced by the number and identity of components that

will be in the agglomerate (and their proportions) as well as, in the case of the components, by the desired size of the agglomerate.

In a 50:50 mixture of two particles, for example,  
5 for at least 90% by volume of the particles the maximum particle size may be 20-30 $\mu$ m, and very often a much smaller size will be appropriate. Once the particle size of one of the components is reduced, the maximum size of another component may be increased.

10 There may also be particular requirements for the size of individual components, so that often the agglomerate will contain components of different sizes.

Colour mixing:

For colour "mixing", that is when two or more  
15 differently coloured components are used, a homogeneous colour in the resulting coating is obtained by utilising sufficiently small particle sizes that the difference in colour of individual particles in the resulting coating is not visible to the naked eye. Theoretical  
20 considerations put this size at no more than 39 $\mu$ m for particles present in a perfect mix. In practice, a perfectly ordered mix is currently unachievable, so the particle size is much less.

This critical size is dependent on a number of  
25 factors, including the contrast in hue and luminance between the different particles and the ratio of the different coloured particles. Luminance is somewhat more

important than hue, so that the critical size is lower for a mixture of black and white particles than for a mixture of different coloured particles of similar luminance. For any pair of coloured powders the critical size is lowest for a 1:1 mixture. The critical size is also very dependent on the nature (randomness) of mixing.

For a 1:1 mixture of black and white particles, the critical size for all the particles is about  $2.5\mu\text{m}$  for a random mixture. If, however, the mixture is a perfect alternating array of black and white particles, the critical size for all the particles is above  $20\mu\text{m}$ . The sensitivity of critical size on going to non-perfect mixtures can be accounted for by the statistical probability of the same colour particles lying adjacent to one another.

For random 1:1 mixtures of blue and yellow particles, the critical size is also about  $2.5\mu\text{m}$ , although this rises to  $5.5\mu\text{m}$  for 9:1 mixtures of blue and yellow and to  $3.3\mu\text{m}$  for 1:9 mixtures. For random 1:1 mixtures of red and yellow particles the critical size is  $3.5\mu\text{m}$ , rising to about  $5.0\mu\text{m}$  for 9:1 and 1:9 mixtures; mixtures of red and blue particles give similar results. Mixtures of white and yellow particles have a critical size in the range of 10 to  $15\mu\text{m}$ . Mixtures having three or more coloured components generally have a critical size which is similar to or larger than that of

mixtures of two of the components.

For certain combinations of colour, however, satisfactory mixing to produce a homogeneous colour has proved practicable with 25 $\mu$ m particles, especially when  
5 dark shades and shades of similar hue (for example, dark bluey-green and dark greeny-blue) are mixed.

- Suitably, for colour mixing, at least 90% by volume of the particles of each component have a particle size  $\leq$  25 $\mu$ m, for example  $\leq$  22 $\mu$ m, advantageously  $<$  20 $\mu$ m.
- 10 Preferably this limit is  $\leq$  15 $\mu$ m, advantageously  $\leq$  10 $\mu$ m, for example  $\leq$  8 $\mu$ m, for example  $\leq$  5 $\mu$ m, and usually for example  $\geq$  0.5 $\mu$ m, advantageously  $\geq$  2 $\mu$ m, preferably  $\geq$  4 $\mu$ m, more especially  $\geq$  5 $\mu$ m, for example substantially 10 $\mu$ m or substantially 5 $\mu$ m. 90% by volume of particles in the  
15 ranges 0.5-10 $\mu$ m, 2-5 $\mu$ m, 5-10 $\mu$ m, 4-8 $\mu$ m and 2-8 $\mu$ m should be mentioned. Components in which at least 75% by volume of the particles have such particle sizes should also be mentioned. Generally, no more than 1% by volume should be above 35 $\mu$ m and usually all should be below 39 $\mu$ m.
- 20 Thus, for example, for a homogeneous result the particle size of the colour components is advantageously in the range of 0.5 to 15 $\mu$ m, preferably 5 to 10 $\mu$ m, or 2 to 5 $\mu$ m, with the maximum dimension of at least 99% by weight of the particles preferably being in this size  
25 range; preferably all the particles have a maximum dimension of 10 $\mu$ m or below.

Advantageously the mean particle size for the colour

components for colour mixing is within the range of from 1.5 to 12 $\mu$ m, for example 1.5 to 8 $\mu$ m. However, mean sizes in the range of from 2 to 8 $\mu$ m, for example 2 to 6 $\mu$ m, and in the range of from 8 to 12 $\mu$ m are especially useful.

5 Mean sizes  $\geq 3\mu$ m and  $\leq 5\mu$ m should also be mentioned.

It may be convenient to have available standard batches of individual components, for agglomeration for particular uses as and when required. Hence, even where there is no colour mixing, a coloured component used in  
10 preparing fused composite particles may have the above particle size.

Speckled finishes:

Alternatively, a speckled finish may be obtained by mixing particles having a size greater than those  
15 discussed above. Thus, according to this embodiment of the present invention, the agglomerate comprises components of reduced-sized particles which are nevertheless large enough that when applied to a substrate they are separately visible in the coating; particle sizes  $> 20\mu$ m  
20 should be mentioned. However, the particle size should be such that the resultant agglomerate of two or more such particles is of a suitable size to meet the requirements for application and film thickness. The desired effect is a film constructed of several individual  
25 coloured particle types such that a speckled finish is reproducible and resistant to segregation. At present speckled finishes can only be made by dry-blending normal

particle-sized finished powders and these are susceptible to segregation on transport and application, due to differences in particle size distributions, particle density or chargeability and they therefore give non-reproducible finishes.

Suitably, for a speckled finish, in each component at least 90% by volume of the particles are  $<50\mu\text{m}$  and more than 10% by volume of the particles are  $\geq 20\mu\text{m}$  and the mean particle size is in the range of from 15 to  $35\mu\text{m}$ , more especially 20 to  $30\mu\text{m}$ , for example substantially  $25\mu\text{m}$ . Preferably, less than 10% by volume are  $<10\mu\text{m}$ .

"Sooty" powders - colour correction:

The agglomeration bonding technique of the present invention may also be used for colour tinting or correction of the colour of a batch. Thus, if a ready-made coloured powder is found to be failing, a colour specification it may be corrected by the addition of one or more coloured film-forming components or pigment(s).

In the past, colour correction was carried out by adding dry pigments and re-extruding the powder. The re-extrusion and the increased solids:binder ratio may, however, change the film characteristics. By using a coloured film-forming component or pigment component (or single pigment mass tones) and adding either by an agglomeration method according to the present invention, the solids:binder ratio is not dramatically altered and



the additional processing is less severe.

Thus, according to a different embodiment of the present invention, the agglomerate comprises larger-sized (for example, conventionally-sized) coloured film-forming  
5 particles and smaller coloured film-forming or pigment particles, for example the reduced-size film-forming particles detailed above for colour mixing, used in amounts preferably of up to 5% by weight, e.g. up to 1% by weight, for example up to 0.5% by weight, more  
10 particularly up to 0.3% by weight, to displace the colour of the larger-sized component over a small colour region, this being used for colour tinting or colour correction of a batch. The amount and size of the smaller particles should be such that they are individually not visible in  
15 the resulting film. This would allow for correction of colour within a batch without the need for re-extrusion.

Suitably, the larger-sized particles in the agglomerate are more than 10% by volume  $\geq 50\mu\text{m}$ , and more usually no more than 70%  $< 50\mu\text{m}$ , with a mean particle  
20 size 15 to  $75\mu\text{m}$ , more usually 25 to  $50\mu\text{m}$ , preferably 35 to  $50\mu\text{m}$ , and the smaller-sized particles are at least 90% by volume  $< 20\mu\text{m}$ , preferably  $< 10\mu\text{m}$ . Advantageously, all the smaller component particles are  $< 25\mu\text{m}$  and no more than 3% are  $< 1\mu\text{m}$ . Advantageously, the mean particle size  
25 of this component is within the range of from 1.5 to  $12\mu\text{m}$ , for example 2 to  $8\mu\text{m}$ , preferably 2 to  $6\mu\text{m}$  or 8 to  $12\mu\text{m}$ ; mean sizes  $\geq 3\mu\text{m}$  and  $\leq 5\mu\text{m}$  should especially be

mentioned.

Size of other additives:

An agglomerate of the present invention may also include a special non-film-forming additive(s) as detailed above, and these may be 90% by volume  $\leq 30\mu\text{m}$ , more especially 20-30 $\mu\text{m}$ , for example substantially 25 $\mu\text{m}$ , in size. Additives with 90% by volume having a size  $\leq 25\mu\text{m}$ , or 20-25 $\mu\text{m}$ , should especially be mentioned. The size of the additive(s) is dictated, however, not only by the size requirements for the agglomerate (influenced inter alia by the requirements for the resulting film), but also by their specific identity and function. For example, a particle  $> 10\mu\text{m}$  in size may produce a visible effect; generally, at least 90% by volume of the component should be below 10 $\mu\text{m}$  to avoid this. Thus, for example, a large-scale texturing effect may be obtained with sand or other inorganic particles at 90% by volume  $> 10\mu\text{m}$ ; when an uncoloured compatible film-forming component is used for adjusting resin content, it is preferably  $> 90\%$  by volume  $< 20\mu\text{m}$ , more especially  $> 90\%$   $< 10\mu\text{m}$  as for colour mixing, in order to avoid being separately visible in the resulting coating.

Incompatible film-forming components for matting/  
texturing or surface segregation; non-film-forming  
components for matting or texturing

As has been mentioned above, an incompatible film-forming component may be used to provide gloss reduction

or texture, or it may be used to obtain a multilayer system.

For a matting effect, discrete domains must be present during film-formation. Thus, as indicated above, 5 components should be incompatible (immiscible) with each other during film-formation; for gloss reduction a difference in surface tension is highly desirable, especially if the domain size is small or if the principal film former is of high molecular weight; for 10 really good results with such systems, and for texturing, a difference in surface tension is probably essential.

With a small domain size, the incompatibility effect achieved generally becomes more pronounced, but with too small a domain size with respect to the wavelength of 15 light, gloss increases.

Film-forming components of similar chemistry but different gel times provide incompatibility during film-formation, but for provision of different surface tensions, a non-film-forming polymer or a film-forming 20 polymer of different chemistry from the principal film-forming polymer, incompatible therewith before curing, is required. An example of the latter is the use of two different thermosetting polymer components such as polyester and acrylic. When the film-forming components 25 have different surface tensions, segregation occurs and enhances matting, so that there is a greater gloss reduction at the same level of addition of second

component, or, for the same effect, the level of addition is less.

The difference in surface tension aids transport of one component to the surface. This component will tend  
5 to stratify if the discrete particles start to coalesce, and ultimately a continuous film is produced; whether or not the component coalesces depends on its viscosity and on surface tension: low viscosity and/or low surface tension enhance the tendency to coalesce.

10 For example, an incompatible film-forming component of relatively small particle size may be used to provide a reduced-gloss finish. The nature of the finish varies according to the size of the first film-forming component and the proportions of components. With a polyester  
15 component of conventional size and 10% by volume of reduced sized acrylic component, for example, we have obtained a textured matt finish; with the same sizes, but half the amount of acrylic, a "cracked-ice" effect was obtained, and with 10% by volume of reduced-sized  
20 acrylic component and a polyester component also of small particle size, a non-textured matt finish was obtained.

Thus, for example, in one embodiment of the present invention the agglomerate comprises a film-forming component of any particle size, but preferably having at  
25 least 90% by volume of particles  $< 20\mu\text{m}$  and with a preferred mean particle size in the range of from 1.5 to  $12\mu\text{m}$ , especially 3 to  $5\mu\text{m}$  or 8 to  $12\mu\text{m}$ , and an

incompatible film-forming component having at least 90% by volume of particles  $< 20\mu\text{m}$ , more especially at least 90% by volume  $< 10\mu\text{m}$ , and with a preferred mean particle size in the range of from 1.5 to  $12\mu\text{m}$ , for example 3 to 5  $5\mu\text{m}$  or 8 to  $12\mu\text{m}$ .

Increases in the quantity of the acrylic component i.e.  $> 10\%$  leads to segregation/stratification of the acrylic component at the air interface as evidenced by increasing gloss. The kinetics of this process can be enhanced by using a larger-sized acrylic particle. The degree of stratification occurring depends on the particle size of both the polyester and acrylic particles.

For increased surface separation for multilayer finishes, we believe the particle size in each of the two (incompatible) components needs to be larger, probably approaching the maximum size commensurate with forming a suitable agglomerate.

Suitably, for such multilayer systems, in each component at least 90% by volume of the particles are  $< 50\mu\text{m}$  and more than 10% by volume of the particles are  $\geq 20\mu\text{m}$  and the mean particle size is in the range of from 15 to  $35\mu\text{m}$ , more especially 20 to  $30\mu\text{m}$ , for example substantially  $25\mu\text{m}$ . Preferably, less than 10% by volume are  $< 10\mu\text{m}$ .

The additive PTFE, a non-film-forming polymer, has been mentioned as a texturing agent and as a gloss-

reducing additive (and as a friction-reducing additive). Whether a texturing or a matting result is obtained is influenced by the particle size.

For example, if medium-sized or relatively large  
5 particles of PTFE are agglomerated with small or relatively small film-forming particles, or medium-sized particles with medium-sized particles, a textured finish is obtained. Thus, for example, in one embodiment, the PTFE has at least 90% by volume of its particles  $< 50\mu\text{m}$ ,  
10 more than 10% by volume  $\geq 20\mu\text{m}$  and a mean particle size in the range of from 15 to  $35\mu\text{m}$ , and the film-forming component has at least 90% by volume of particles  $< 20\mu\text{m}$ , and preferably a mean particle size in the range of from 1.5 to  $12\mu\text{m}$ , especially 3 to  $5\mu\text{m}$  or 8 to  $12\mu\text{m}$ .

15 However, with smaller particle sizes of the PTFE, the size of the texture is reduced and, when the deformations become sufficiently small, reduced-gloss finishes are obtained.

Similar texturing or gloss-reducing effects at  
20 different particle sizes are obtained with CAB, Acronal (Trade Mark) and cross-linked polymers.

Various agglomerate types:

In order to assist in understanding the ramifications and the potential of the fused agglomerates of the  
25 present invention, conceptual agglomerates composed of several different combinations of component sizes may be mentioned.

- (I) The agglomerate comprises a larger-sized film-forming component and one or more smaller-sized components, usually a small-sized or relatively small-sized film-forming or non-film-forming component or two or more components of such a size; an example of such a system is the colour correction system described above.
- (II) The agglomerate comprises two medium-sized components, at least one of which is film-forming, as, for example, in the speckled finish or multilayer system described above; additional small or relatively small-sized components may also be present.
- (III) The agglomerate comprises two or more small or relatively small-sized components, at least one of which is film-forming, as in the colour mixing system or matt system described above.
- (IIIA) The agglomerate comprises a large or medium-sized component and one or more smaller-sized components, at least one of the smaller-sized components being film-forming, as, for example, in the textured finish described above.

More especially, these agglomerate types have particle sizes as follows:

- 25 (I) Component (i): more than 10% by vol.  $\geq 50\mu\text{m}$   
preferred mean particle size  
25-50 $\mu\text{m}$

- Each component (ii): at least 90% by vol. <20 $\mu$ m  
preferred mean particle size  
1.5-12 $\mu$ m
- 5 (II) Each component: at least 90% by vol. <50 $\mu$ m  
more than 10% by vol.  $\geq$ 20 $\mu$ m  
mean particle size 15-35 $\mu$ m
- (III) Each component: at least 90% by vol. <20 $\mu$ m  
preferred mean particle size  
1.5-12 $\mu$ m
- 10 (IIIA) Component (i): moderate size, e.g.  
at least 90% by vol. <50 $\mu$ m  
more than 10% by vol.  $\geq$ 20 $\mu$ m  
mean particle size 15-35 $\mu$ m,  
or large-sized
- 15 Each component (ii): at least 90% by volume <20 $\mu$ m  
preferred mean particle size  
1.5-12 $\mu$ m

Preferably, components in type III agglomerates and small-sized components (ii) in types I and IIIA

20 agglomerates have particle sizes at least 90% by volume < 15 $\mu$ m, more especially < 10 $\mu$ m, often < 2 $\mu$ m. Usually all particles are < 25 $\mu$ m and, in a film-forming component, a maximum, for example, of 3% by volume may be < 1 $\mu$ m.

Preferred mean particle sizes are usually in the range of

25 from 1.5 to 12 $\mu$ m, for example 1.5 to 8 $\mu$ m, preferably 2 to 8 $\mu$ m, for example 2 to 6  $\mu$ m, more especially 3 to 5 $\mu$ m, or 8 to 12 $\mu$ m.



Preferably, components in type II agglomerates and moderate-sized components (i) in type IIIA agglomerates have particle sizes at least 90% by volume substantially 25 $\mu$ m and preferably also less than 10% by volume < 10 $\mu$ m.

- 5 Preferred mean particle sizes are in the range of from 20 to 30 $\mu$ m, more especially substantially 25 $\mu$ m. Large-sized components in type IIIA agglomerates may be of some considerable size, depending on the effect desired; examples are metallic pigments and sand where the  
10 additive cannot be size-reduced without loss of function.

Preferably, large-sized components (i) in type I agglomerates are conventionally-sized powder coating particles. Generally, the components have at least 90% by volume in the range of from 20 to 100 $\mu$ m and no more  
15 than 70% by volume < 50 $\mu$ m, with a mean particle size usually at least 35 $\mu$ m, for example in the range of from 35 to 60 $\mu$ m, more often 35 to 55 $\mu$ m, for example 35 to 50 $\mu$ m. Alternatively, reduced-sized components may be used, and particle sizes, for example, at least 90% by  
20 volume < 70 $\mu$ m, for example at least 90% < 60 $\mu$ m, or at least 90% < 50 $\mu$ m, should be mentioned. Preferred mean particle sizes are in the range of from 25 to 55 $\mu$ m, more especially, 25 to 50 $\mu$ m. Thus, for example, the component may be fluidisable alone.

- 25 Film-forming components in type II agglomerates or in type III agglomerates preferably have the same or similar particle size distributions.

Fillers and other inert particles used to produce gloss reduction or texturing, texturing agents (e.g. PTFE, CAB, Acronal 4F (Trade Mark)), fibres and, especially metallic pigments and mica, and abrasives  
5 (especially sand and metal carbides) usually are relatively large particles, and may therefore be incorporated in agglomerates of type II or type IIIA (where they are the larger-sized component).

The particle sizes quoted for the various grades of  
10 mica pigments are 5-20 $\mu$ m, <15 $\mu$ m, 10-50 $\mu$ m, 10-60 $\mu$ m, 5-100 $\mu$ m, 30-100 $\mu$ m, 40-200 $\mu$ m, 5-50 $\mu$ m, 10-100 $\mu$ m. From the data available it would appear that the various grades of aluminium pigments have similar particle sizes to the mica pigments.

15 The size of those additives giving a texture or hammer finish is influenced by their aesthetic function, and may be, for example, 20-30 $\mu$ m for CAB used with a metallic pigment to achieve a hammer finish; reduction to a much smaller particle size could adversely affect or  
20 even destroy their ability to produce the desired appearance. Other texturing agents are generally conventionally of fine particle size; CAB, Acronal or PTFE, for example, may be used as the smaller component in a type I agglomerate, for example in an amount of < 2%  
25 by volume, usually about 1% by volume. At larger particle size CAB and Acronal may be used to achieve novel texturing effects.

It should be noted that for a non-slip surface a smooth film is not required, and, whilst covering by the binder is required, projection of part of the sand or other additive above the surface is not only allowable, but desired (removing one constraint on the component size). Particles of some considerable size (e.g. about 150 $\mu$ m) could be agglomerated provided they were a small proportion of the mixture. In such cases the sand will be the larger-sized component in a type IIIA agglomerate. Sand of rather smaller particle size may of course be used for gloss-reduction or texturing.

Pigments, heterogeneous catalysts, rubber tougheners, catalysts, biological material, intumescent and thermochromic pigments, and tribocharging and corona-charging additives are usually required in only small amounts relative to the film-forming component (for example tribocharging additives may be added at 2% or less, usually 1% or less, catalysts also at 2% or less) and/or are effective at small particle size (for example, rubber tougheners are effective at about 1 $\mu$ m size).

These are therefore usually present in the agglomerate as relatively small particles, and may therefore be incorporated in agglomerates of types I, III and IIIA (where they are a smaller-sized component).

For rubber tougheners, incorporation in a type III agglomerate should especially be mentioned.

Texturing agents such as PTFE, CAB and Acronal, if

used as very small particles in, for example, type I and III agglomerates, may have a gloss-reducing effect.

Microcapsules, friction-reducing additives, non-film-forming matting polymers and other gloss-reducing agents, fillers and/or extenders used as partial replacement for resin, silicone non-stick substances and anti-adhesives and water-soluble products for introducing porosity may be used in various particle sizes, and may therefore be incorporated in agglomerates of types I, II, III and IIIA. In type II and IIIA agglomerates fillers and/or extenders will also produce a reduction in gloss as mentioned above.

As an alternative to its use in microcapsules, zinc, which unless encapsulated would cause problems because of its conductivity, may be present as the large component in the type IIIA agglomerate; it is thus effectively encapsulated by the smaller film-forming component.

Friction-reducing additives may range in size, for example, from 1 to 30 $\mu$ m or more, more especially from 2 to 30 $\mu$ m. Excellent results have been obtained with particles 25 $\mu$ m in diameter.

Incorporation of silicone non-stick substances and anti-adhesives in a type II agglomerate and of microcapsules in types I and II agglomerates should especially be mentioned.

The size of sodium chloride or other water-soluble component for the preparation of porous coatings should

be chosen carefully, and depends on the size of pores required and on the properties of the coating required, for example water vapour transmission rate, oxygen transmission rate, etc.. Types II and III agglomerates  
5 should especially be mentioned.

Reference has already been made to the use of epoxy and PVDF systems. The PVDF may be the inner particle in a type IIIA or type I agglomerate, with a very small amount of epoxy; on film-formation some epoxy migrates  
10 to the surface, where it degrades quickly, causing a rapid but minor loss of gloss. The remaining epoxy serves to promote adhesion of the PVDF to the substrate, and also assists the charging and charge retention of the powder and its application to the substrate.

15 The quantity of any performance or aesthetics additive in the agglomerate is dependent on the effect desired and also on the structure of the agglomerate, including the particular sizes of the components.

For example, with a type I agglomerate there may, for  
20 example, be on average no more than one layer of small particles per large particle and preferably the large particle should be completely coated. With too large a quantity of additive, the quality of mixing decreases.

Thus, for example, in a type I agglomerate each  
25 additive to the larger-sized component may be present in an amount of up to 2% by volume of the total agglomerate. The total amount of such additive(s) may be, for example,

up to 30% by volume.

In a type II agglomerate there may be, for example, at least 20%, preferably at least 30%, by volume of each component, and usually 30 to 50% of additive for a two-  
5 component system.

In a type III or IIIA agglomerate there may, for example, be up to 30% by volume of non-film-forming component or components in total.

Speckled agglomerates are possible with a type IIIA  
10 agglomerate, as well as with a type II agglomerate, and for these and for colour correction with type I agglomerates and type III agglomerates used for colour mixing, the proportions of film-forming components depend on the desired appearance.

15 Fillers in general should constitute no more than 30% by volume of the agglomerate, preferably no more than 20%, and preferably the filler and pigment together are no more than 30% by volume; usually the filler itself is no more than 5% by volume.

20 Similarly, for example, a coloured or uncoloured incompatible film-forming component used as matting base in any agglomerate type may be up to 30%, preferably up to 20%, more especially up to 15% by volume of the total agglomerate, and more especially at least 5% by volume.

25 With < 5% by volume of incompatible film-forming component a textured finish may be produced. Non-film-forming polymers are suitably up to 20%, preferably up to

10%, for example up to 5% by volume, of total agglomerate. Conventional gloss-reducing additives may be up to 10%, for example up to 5%, by volume of the agglomerate.

5       With increasing amount of acrylic component, the gloss of a polyester, epoxy, polyester-epoxy or polyurethane film increases because the acrylic component tends to coalesce; the extent of gloss increase/coalescence is a function of the concentration of the  
10 component and the speed at which it can reach the surface, itself a function of its initial size and of its surface tension versus viscous drag from the surrounding principal film-forming component.

      In a multilayer system, the ratios of segregating  
15 components may be, for example, from 90:10 to 50:50, advantageously at least 85:15, preferably 80:20 to 50:50, especially at least 75:25, for example at least 70:30, for example substantially 70:30.

      The present invention especially provides a composition  
20 suitable for application as a powder coating and which is in the form of a fused agglomerate of different particulate components comprising a primary film-forming component and a second film-forming or non-film-forming component, the identity, amount and particle size of  
25 these components being such that when the powder coating is applied to a substrate and heated to form a continuous coating the components are incompatible and a matting

effect is obtained.

The present invention further provides a composition suitable for application as a powder coating and which is in the form of a fused agglomerate of different particulate components comprising a primary film-forming component and a second film-forming component incompatible with the principal film-forming component, the identity, amount and particle size of these components being such that when the powder coating is applied to a substrate and heated to form a continuous coating the two components segregate and form a multilayer system.

#### Composition of film-forming systems

A film-forming resin may be a thermosetting resin or a thermoplastic resin. When a thermosetting resin is used, the solid polymeric binder system generally includes a solid curing agent for the thermosetting resin; alternatively two co-reactive film-forming thermosetting resins may be used.

Except where otherwise required for special effect or result, two or more film-forming components (whether coloured or non-coloured) should have similar melting point, melt viscosity, surface tension and other rheological properties, so that they flow and level to the same extent when the powder coating is applied to a substrate, and except where otherwise required for surface segregation any two or more film-forming components are preferably based on the same binder system,



usually of similar composition except for the pigmentation or gel time.

Examples of pigments which may be used in the basic film-forming components or as separate components are

5 inorganic pigments, such as, for example, titanium dioxide white, red and yellow iron oxides, scarlet chrome, chrome yellow and carbon black, and organic pigments such as, for example, phthalocyanine, azo, anthraquinone, thioindigo, isodibenzanthrone,

10 triphenhdioxane and quinacridone pigments, vat dye pigments and lakes of acid, basic and mordant dyestuffs. Dyes may be used instead of or as well as pigments. Each coloured film-forming component of the coating composition may contain a single colorant (pigment or dye) or

15 may contain more than one colorant.

A pigment content of < 40% by weight of the total pigment and filler content (the filler being added to assist opacity, while keeping costs down) may be used. Usually a pigment content of 25-30% is used, although

20 opacity can be obtained with dark colours with < 10% by weight of pigment.

The powder coating composition may, for example, be based on a solid polymeric binder system comprising a carboxy-functional polyester film-forming resin used with

25 an epoxy-functional curing agent such as, for example, an epoxy resin, for example a condensed glycidyl ether of bisphenol A, or a low molecular weight tri-functional

epoxy compound such as, for example, triglycidyl isocyanurate, or with a beta-hydroxyalkylamide; or a hydroxy-functional polyester used with an isocyanate-functional curing agent; or an epoxy resin used with an amine-  
5 functional curing agent such as for example, dicyandimide; or a functional acrylic resin, for example a carboxy-, hydroxy- or epoxy-functional resin, used with an appropriate curing agent. The binder may be a thermoplastic resin such as, for example, a fluoro-resin, for  
10 example polyvinylidene fluoride or an ethylene/tetrafluoroethylene copolymer, or poly-phenylene sulphide.

Mixtures of co-extruded film-forming binders may be used; for example a carboxy-functional polyester may be used with a carboxy-functional acrylic resin and a curing  
15 agent such as, for example, a beta-hydroxyalkylamide which serves to cure both polymers.

One or more additives such as, for example, a flow-promoting agent, a plasticiser, a stabiliser, for example a stabiliser against UV degradation, or a filler, or two  
20 or more such additives may be present in the coating composition, being mixed with a film-forming component(s) before or in the extruder, or present as separate components in the agglomerate. Some additives, however, are unsuitable for co-extruding and must be present as  
25 separate components.

#### Preparation of the agglomerates

The film-forming component(s) and non-film-forming

component(s) where appropriate may be prepared by methods generally known in the production of powder coatings, where appropriate with a final comminution step which produces a low particle size.

5        In general, the film-forming and non-film-forming particles may be of any shape; for example they need not be spherical. Fibres, microcapsules, slip and non-slip additives and metallics, however, are generally of specific shape.

10        The comminution may be carried out, for example, by jet milling in a fluid energy mill. Fluid energy mills function by collision of particles in a high velocity stream of gas, generally air. Particles of diameter less than  $5\mu\text{m}$  are easily obtained from a feedstock of mean  
15        particle size  $50\mu\text{m}$ . Fluid energy mills have the advantage that the composition is continuously cooled by the gas stream. In an alternative process the individual component, preferably at particle size below  $500\mu\text{m}$ , may be dispersed in a non-solvent for the ingredients of the  
20        component, for example water, and comminuted by techniques known for wet paint, for example in a high speed bead mill or ball mill. Conventional comminuting devices using metal shearing blades are less efficient in producing sub- $10\mu\text{m}$  particles as it is difficult to  
25        prevent fusion of the heat-sensitive powder.

Mixing of the various components may be carried out by various techniques.

A preferred method for mixing film-forming and other particles is dry mixing of the powders in a high-shear mixer. Powders of particle size below  $15\mu\text{m}$ , for example 0.5 to  $10\mu\text{m}$ , behave as cohesive non-aeratable powders.

5 Devices containing a high shear chopper, for example, produce satisfactory mixtures of substantially all components of this particle size. High-speed forces may be required to break unwanted agglomerates of particles formed on storage and handling of the components.

10 A simple example of a suitable high-shear mixer is a modification of the type of food mixer known as a liquidiser. An inlet is arranged in the mixing chamber at about the level of the rotating blade. The inlet is for a high-velocity gas stream, preferably air, to ensure  
15 that the powder is kept circulating past the blades. Another example of a suitable high-shear mixer is described in GB Patent 2132128 in which a disintegrator or chopper rotating about the horizontal axis is positioned above a disc rotating about a vertical axis  
20 which acts as the main agitator for the mixer. Mixers of this type are sold by Freund Industrial Co. Ltd.

In further examples of suitable high-speed mixers blades of paddles are mounted in a cylinder to rotate about the axis of the cylinder and to scrape the inner  
25 surface of the cylinder so that all the powder being mixed is continuously moved around and along the cylinder. The blades may be in the shape of ploughshares

to improve mixing of the powder along the length of the cylinder. Chopper blades are mounted about half way along the cylinder to rotate at right angles to the axis of the cylinder. Such mixers are the Herfeld mixer and  
5 that sold by Lodige-Morton Machines Ltd. as the 'Lodige Ploughshare' mixer and by Winkworth Engineering Ltd. under the trade name 'RT Mixer'.

Alternatively, comminuting of film-forming component(s) and other component(s), where appropriate, and  
10 mixing may be carried out simultaneously by feeding a mixture of components to a comminuting apparatus such as, for example, a fluid energy mill, or by feeding such a mixture in aqueous dispersion to a bead mill or ball mill. There may be problems in cleaning the comminuting  
15 apparatus used in this process, particularly if using wet grinding.

In an alternative mixing process the film-forming and other components where appropriate are mixed by an electrostatic mixing technique. In this process a powder  
20 component, for example the colour component, is electrically charged and a second component, for example an uncoloured or second colour component, is not charged or is charged to a different potential, and the powders are mixed. For example, one powder may be electrically  
25 charged positively and another powder may be electrically charged negatively. Since the charged particles combine with oppositely charged particles or uncharged particles

preferentially, electrostatic mixing may produce an agglomerated product approaching a perfect mixture rather than a random mixture, thus, where colour is a factor, allowing higher particle sizes to be used than with other forms of mixing; for example, particle sizes of up to 20 $\mu$ m for the film-forming powders may be used, even with light and/or dissimilar shades, although particle sizes in the range 1.5 to 10 $\mu$ m are preferred. The charged particles may be allowed to combine freely or may be mixed in a pulsed electric feed. A suitable apparatus for electrostatic mixing of powders is described by C.L. Tucker and N.P. Suh in 'Polymer Engineering and Science', October 1976, Vol. 16, at pages 657 to 663.

When three or more powders have to be mixed, for example, two coloured powders and an uncoloured powder or three coloured powders, they are preferably mixed sequentially when electrostatic mixing is used. Alternatively the three or more powders may be charged to different potentials and combined in one mixing operation. For example, if three powders are to be mixed, one may be charged positively, one negatively and the third may be uncharged.

Agglomeration to produce a product with fused composite particles large enough that the material is air-fluidisable and can be applied to the substrate by conventional electrostatic spray, usually 15-100 $\mu$ m and preferably 25 to 50 $\mu$ m, may be achieved in a number of

ways.

One agglomeration process is granulation in which an added material is used to promote adhesion between the particles.

- 5        A granulating agent may be added as a solution, but it is important that the solvent does not affect the coating composition. A preferred solvent for the granulating agent is water. The non-volatile constituents in the granulating agent are preferably
- 10 compatible with the resin in the coating composition. Thus, for an acrylic-based powder coating, a water-borne acrylic granulating agent can be used, such as, for example, Glascol HA2 obtainable from Allied Colloids Ltd. This granulating agent is also suitable for use with
- 15 thermosetting polyester powder coatings. The granulating agent for an epoxy-based powder coating may, for example, be a water-based epoxy resin. A water-soluble cellulose ether such as, for example, that sold under the Trade Mark "Celacol M20P" is an alternative granulating
- 20 agent for polyester, acrylic or epoxy resins. The granulating agent may be in the form of a latex, for example a vinyl or acrylic polymer latex. Typically the amount of granulating agent required is less than 15% by weight, for example 1 to 10%, based on non-volatile
- 25 solids, to agglomerate powder with a mean particle size  $5\mu\text{m}$  to yield a product of mean size  $40\mu\text{m}$ .

Alternatively, a chemically-harmless solvent for the

binder may be used as granulating agent. The solvent need not be a good solvent for the film-forming components and is preferably quite volatile to aid extraction after agglomeration. An example is methanol (and  
5 many other simple alcohols), CFCs, liquid CO<sub>2</sub> and chlorocarbons, especially methylene chloride. Vacuum extraction can be used to aid removal of the solvent after agglomeration.

The granulating agent is preferably introduced as a  
10 spray into a mobile mixture. It may for example be so introduced into the apparatus of U.K. Patent 2132128, or into a 'Lodige Ploughshare' or 'Winkworth RT' mixer at a position about half way along the mixing cylinder. When the same machine is used for mixing and agglomerating in  
15 this way, dry mixing, if required, should be carried out before addition of the granulating agent. The high-shear chopper is generally not used during granulation, or is used at a much reduced speed. We have found that finely atomised granulating agent allows better control on the  
20 product particle size distribution and more efficient use of the granulating agent.

An alternative apparatus which can be used for both mixing and granulating is the 'Spectrum' sold by T.K. Fielder and Co. Ltd. This is of the type having a  
25 chopper rotating on a vertical plane above an agitator rotating in a horizontal plane. An aqueous granulating agent may be added after mixing, and the apparatus is



equipped with microwave generators of a frequency to heat the water added with the granulating agent, thus drying to the granulated product.

In an alternative process for introducing the granulating agent, the granulating agent may be encapsulated in particles of the film-forming resin. An aqueous solution of the granulating agent may be emulsified in a solution of the film-forming resin in an organic solvent, for example a solution of a polyether binder resin in a chlorinated hydrocarbon such as, for example, chloroform. The emulsion is spray-dried to form capsules of the desired particle size, for example 1.5 to 10 $\mu$ m. These capsules are added to the other component(s) either at the start of mixing or during mixing. The capsules are gradually broken by the shearing forces used in mixing, release the granulating agent solution to cause granulation.

The agglomerated mixture is preferably dried before it is discharged from the mixer to prevent undesired subsequent agglomeration. A drying gas, for example dry air at 25-80°C, may be passed through the mixer after the granulating agent has been thoroughly mixed into the powder coating composition. The mixing action is preferably continued during drying. Alternatively, the agglomerated mixture may be dried in a fluidised bed dryer after discharge from the mixer.

An alternative method of fusion agglomeration is to

use mechanical forces to bind the particles through a process involving deformation and microwelding of the plastic material. A commercially available device for carrying out such mechanical agglomeration is sold as the Nara hybridisation system and described in European Patent Application 224659. Another mechanofusion device is sold by Hosokawa Micron B.V. as an Ang mill. A further apparatus suitable for a mechanofusion agglomeration is a mill having conical and planar dies as described in WO-86/04835. We have shown, for instance, that a material having very broad softening range of 45-80°C may be agglomerated using this device.

A further suitable device is the FM10 Henschel mixer. It relies on a vigorous mixing action to heat up the powder, so that the particles are sufficiently softened to bond under relatively mild impact. The FM10 is a 10 litre chamber featuring a single impeller. The speed of rotation is variable, but typically run at 3000 rpm. A thermocouple is located in the mixer chamber to monitor temperature. Typically, 2 Kg of the mixed components are heated to 50-55°C within 7 minutes. At this temperature bonding occurs. We have found that it is especially advantageous to provide an external heat source to circulate hot water through the external jacket of the vessel.

Thus, in one embodiment of the agglomeration process using a modified Henschel mixer, the vessel is

initially cold and empty, the powders to be mixed are charged to the vessel and stirred at high speed for approximately one minute. The stirrer speed is then reduced to "slow" speed and the hot water passed through the jacket to bring the temperature inside the vessel to 60°C; at this temperature agglomeration proceeds fairly swiftly. This stage of the operation takes approximately 30 minutes. The rate of agglomeration is, we believe, controlled by the rate of heat-up, but the heat-up rate is influenced by the tendency of the powder to stick to the inside wall of the vessel. The provision of a wall scraper is useful to deal with this problem. Once agglomeration has been achieved, the powder may be cooled and sieved.

When there is prior electrostatic mixing of powders before agglomeration, the mixed particles are agglomerated by the attraction of oppositely charged particles. It is however necessary to supplement this with subsequent more permanent agglomeration, for example by a granulation process or by heat softening.

The components may alternatively be mixed and agglomerated by dispersing them together in a liquid dispersion medium followed by drying of the dispersion under conditions causing fusion agglomeration. The liquid dispersion medium is preferably a non-solvent for substantially all the ingredients of the powder coating composition. Water is the preferred dispersion medium.

It may be used alone or with a surfactant or water-miscible organic liquid such as, for example, an alcohol or an ether alcohol.

The mixing apparatus used to form the dispersion may  
5 use mechanical means, for example a high-speed mixer which employs a rotating toothed disc to generate high shear forces, or may use ultrasonic dispersion as well as or in addition to the mechanical disperser. For example mixing in a high-speed disperser may be followed by  
10 ultrasonic dispersion.

The process used to disperse the composition in the liquid dispersion medium may also serve as the final step in comminuting binder particles of the powder coating composition to the desired particle size, for example to  
15 below  $10\mu\text{m}$ .

The dispersion produced is fed under pressure to the drying apparatus, for example a spray-drying apparatus. Spray-drying may be carried out using a conventional atomising spray head, in which case the diameter of the  
20 spray head at its narrowest point is preferably  $20\text{--}500\mu\text{m}$  to achieve fused agglomerated particles of the desired particle size for electrostatic spray, namely  $20\text{--}50\mu\text{m}$ . Spray-drying has the advantage that the particle size of the fused agglomerated powder coating composition  
25 produced can be controlled by the concentration of the dispersion and the diameter of the spray head. The spray may alternatively be a centrifugal spray system, for

example a spinning disk spray, or may be an ultrasonic spray. The spray dryer is preferably a co-current dryer in which the direction of the spray is generally downwards and in which a stream of gas, generally air, passes  
5 down the drying chamber in the same general direction as the spray. This stream of gas is preferably at ambient temperature or above. The inlet temperature of the gas may, for example, be 40-120°C. The agglomerated powder coating particles produced collect at the bottom of the  
10 spray drying chamber and may be removed by a suitable valve system. The vapour of the dispersion medium passes upwards and may be vented. Alternatively the whole output of the spray dryer may be passed to a cyclone separator to isolate the agglomerated powder coating.

15 When different colours are to be mixed the process of the invention is preferably carried out in conjunction with a data-storage system containing details of the proportions of the colour components required to make powder coating in different shades so that for a given  
20 shade and size of batch a data processor can calculate the weight of each colour component to be used. Automatic weighing means may be used if desired. A colour computer may be used if desired to calculate the proportions of colour components required to match a sample of  
25 a non-standard shade.

The components may be stored at a reduced particle size, for example below 10 $\mu$ m, and mixed and agglomerated

as required. Alternatively the components may be stored at a high particle size, for example 15-50 $\mu$ m as conventionally used for coatings, to be comminuted if required, mixed and agglomerated as required.

- 5       The most common method for the application of powder is an electrostatic spray gun, and the particle size required for most commercial application equipment is ideally a distribution between 10-120 $\mu$ m with a mean particle size within the range 15-75 $\mu$ m, preferably 25-  
10 50 $\mu$ m. In the electrostatic spray process the powder coating particles are electrostatically charged by the Corona cloud surrounding the outlet of the spray gun, this cloud being generated by the electrode within the spray gun itself. The charged particles are attracted to  
15 the substrate, which is earthed or oppositely charged. Powder coatings may also be applied using tribostatic guns where the powder particles are electrostatically charged by rubbing against the internal winding of the gun. Another method for the application of powder  
20 coatings is the use of fluid beds. In this instance the article to be coated is usually preheated and dipped into the fluid bed of powder, the article is then withdrawn and the powder coating allowed to cure by residual heat or by further baking in an appropriate oven.
- 25       The invention will be further described by way of example with reference to the accompanying diagrammatic drawings of which:

Figure 1 is a diagrammatic section of an apparatus for producing powder coatings by dispersion and spray-drying.

Figure 2 is a diagrammatic section of an apparatus  
5 for mixing powdered components by electrostatic mixing.

Figure 3 is a diagrammatic section of an alternative apparatus for mixing powdered components by electrostatic mixing.

Figure 4 is a diagrammatic section of a mixer for  
10 mechanically mixing powdered components.

Figure 5 is a diagrammatic longitudinal section of an alternative mixer for mechanically mixing powdered components.

Figure 6 is a diagrammatic cross-section of the  
15 mixer of Figure 5 adapted to carry out granulation after mixing.

Figure 7 is a diagrammatic cross-section of an apparatus for mixing and/or granulating film-forming and other components.

20 Figure 8 is a electron microscope photograph of a conventional powder coating composition, and

Figure 9 shows electron microscope photographs of a fused agglomerated powder coating composition.

The apparatus of Figure 1 generally comprises a  
25 mixer indicated generally by the reference numeral 10 and a spray dryer indicated generally by the reference numeral 20. The mixer 10 is a high-speed disperser

having an impeller 11 mounted on a shaft 12 within a vessel 13. The vessel 13 has an inlet 15 for the dispersion medium, for example water, and an inlet 16 controlled by a valve 17 for feeding the components. The powder coating particles are dispersed in the dispersion medium and the dispersion thus formed is pumped through an outlet 18 by a pump 19 to a spray dryer 20.

The spray dryer 20 comprises a vessel 21 containing a downwardly directed atomising spray head 22. The spray-dried powder coating particles fall to the bottom of the vessel 21 and are removed through an outlet 24 controlled by a valve 25. The vapour of the dispersion medium which is evaporated passes upwards at the side of the vessel 21 and is vented at 30. Air is fed to the dryer 20 through an inlet 28 and passes in through a heater 29 and down a central duct 33, forming a co-current flow of heated air around the spray head 22.

The apparatus of Figure 2 as shown is suitable for mixing four powders in three mixing steps carried out successively. The apparatus can be adapted to include further mixing steps if required. The apparatus comprises an inlet 41 for a first component whose particles have been positively charged, for example using an apparatus similar to that described in "Polymer Engineering and Science", October 1976, at page 658, and an inlet 42 for a second component whose particles have been negatively charged or are uncharged. The inlet 42



can be sleeved with an insulating material designed to impart a change to the particles by tribocharging. Polytetrafluoroethylene, for example, will induce a negative charge on the particles. The particles mix at the junction 43 of inlets 41 and 42, and the oppositely charged particles combine. The combined particles pass along conduit 46. An inlet 47 for a third component meets conduit 46 at junction 48. The particles of the third powder are preferably oppositely charged to whichever of the first and second powders is present at greater weight, or if the second powder is uncharged the particles of the third composition can be negatively charged. The combined particles and the particles of the third powder combine at junction 48 and pass to conduit 52, where they are combined with particles of a fourth powder component supplied through inlet 53 meeting conduit 52 at junction 54. The fourth powder is charged oppositely to the net charge of the first three powders. The resulting combined particles pass through conduit 55 and can be collected in a suitable container. These may then be granulated to achieve more secure agglomeration.

The apparatus of Figure 3 comprises three inlets 61, 62 and 63 for first, second and third powders. The inlets all feed a mixing chamber 64. The particles of the first powder component are charged positively; the particles of the second powder component are charged negatively and the particles of the third powder

component composition are uncharged. The particles combine in mixing chamber 64 and pass to conduit 65, whence they can be collected in a suitable container.

The apparatus of Figure 4 is a modified 'Moulinex' 5 (Trade Mark) food blender and comprises a mixing chamber 71 containing a blade 72 extending in two directions and mounted on a spindle 73. The blade can be rotated at high speed by drive motor 74. The blade 72 has a sharp leading edge in the direction of rotation and has an 10 upwardly inclined portion 75 at one side of the blade and a downwardly inclined portion 76 at the other side of the blade. The inclined portions 75 and 76 of the blade 72 are both tapered so that the tips of the blade 72 are sharp points. An inlet 77 for high-velocity air is 15 positioned in the wall of the chamber 71 substantially at the level of the blade 72. The chamber 71 has a cover 78 which retains the powder coating particles but is porous to air. The cover 78 can for example be of sintered thermoplastic material such as polypropylene or 20 of sintered glass. The combined action of rotation of the blade 72 and the high-velocity air keeps all the powder in the mixing chamber 71 in a substantially fluid state and the high shear action of the blade 72 breaks up any powder agglomerates, which tend to fall into the path 25 of rotation of blade 72 because of their greater weight than the non-agglomerated powder particles.

The apparatus of Figure 5 comprises a cylindrical

mixing chamber 81 containing blades 82 mounted on a drive shaft 83, which in use is rotated by a motor (not shown). A chopper 84 consisting of a set of cutting blades 85 mounted on spindle 86 is situated half way along the mixing chamber 81. The spindle 86 is driven by a motor 87 to rotate the cutting blades 85. The blades 82 are shaped with a leading edge 88 tapered in two dimensions to a point 89 to promote mixing of powders along the chamber 81. The trailing edge 90 of the blades 82 is also tapered but not to a point.

The apparatus of Figure 6 is a modification of the apparatus of Figure 5 and the same parts have the same numerals. The apparatus includes two types of inlet for a solution of granulating agent. The mixing chamber 81 is modified to include a top zone 91 within which are located a series of spray heads such as 92 fed by pipe 93 so that the spray heads 92 are outside the path of rotation of the blades 82. A further inlet 94 is positioned about half way along the mixing chamber 81 and has its outlet 95 adjacent to the blades 85 of chopper 84.

In use the apparatus of Figure 6 is charged with the required amount of powder and optionally other additives and is operated as a dry mixer initially. When sufficient mixing time has elapsed to obtain a random mixture of particles, a granulation agent is introduced through inlets 93 and 94 and the mixing action is continued to

obtain agglomerated composite particles. After addition of the granulation agent is complete, warm dry air is fed to the mixing chamber 81 through inlets 93 and 94 to dry the powder gradually as it is being agglomerated,

- 5 limiting the size of the composite particles formed.

The apparatus of Figure 7 is a modified 'Kenwood A516/517' (Trade Mark) food mixer and comprises a motor 101, contained in a housing 102, which drives a stirrer blade 103 within a mixing chamber 104. An air inlet 105  
10 leads to an inlet chamber 106, separated from the mixing chamber 104 by a glass sinter 107. High-velocity air can be fed to the inlet 105 to fluidise the powdered material in chamber 104 and warm air can be fed to cause drying during granulation. The product is prevented from  
15 escaping during mixing or granulation by a second sintered screen 108 which separates product from exhaust air.

As can be seen from comparison of Figures 8 and 9, (where the size of magnification is shown by each of the  
20 white or black scale bars) a fused agglomerate of the present invention is essentially different from a conventional powder. In Figure 8 the powder is > 10% by volume  $\geq 50\mu\text{m}$ , > 90% by volume  $< 70\mu\text{m}$ , < 70% by volume  $< 50\mu\text{m}$  and mean particle size 35-50 $\mu\text{m}$ ; Figure 9 shows  
25 the result of agglomerating particles 90% by volume  $< 10\mu\text{m}$  in size.

The following Examples illustrate the invention.

ExamplesHydraulic press method for agglomeration

Agglomeration of particles is achieved by the combination of pressure and temperature.

5 Apparatus:

Moulinex Blender

Moore Hydraulic Press

Steel Press Mould

Moulinex Coffee Grinder

10 Endecotts 106 Micron Laboratory Test Sieve

Procedure:

The appropriate samples are obtained in the desired ratios. Mixing is achieved by two fifteen second runs in a Moulinex blender with scrape-down of the blender's  
15 sides between runs. The mixed sample is then transferred to the hydraulic press.

The top and bottom heating plates have a temperature setting of 80°C. The press mould is held between these plates for 45 minutes to allow it to equilibrate from  
20 room temperature. Once equilibrated, the bottom half of the mould is lowered to allow the sample to be inserted. Between the sample and the press mould a thin film of non-stick material (PTFE film) is placed to prevent sample adhesion to the mould. The sample is then placed  
25 in the centre of the mould and covered with another non-stick film.

The press mould is then closed and the hydraulic

loading is, as swiftly as possible, increased to 20 Tons. This maximum loading is maintained for 30 seconds before being released and the agglomerated sample removed from between the non-stick layers.

- 5        The range in applied pressures is  $3 \times 10^6$  to  $7 \times 10^6$  NM<sup>-2</sup>.

The press mould should be closed and allowed to re-equilibrate for 10 minutes prior to re-use.

- 10       The agglomerated sample has the form of a flat, circular cake. This is micronised by insertion into a Moulinex Coffee Grinder for approximately 20-40 seconds.

- 15       The micronised powder is then sieved through an Endecotts 106  $\mu$ m laboratory test sieve and collected. The final powder generally has a particle size distribution of 90% < 120 $\mu$ m and no more than 10% < 10  $\mu$ m.

#### Assessment method for electrostatic separation

An assessment technique for the degree of separation in an agglomerated sample and its dry-blended equivalent is listed below.

20    Apparatus:

Volstatic electrostatic gun  
Extracted spray booth  
Stoving oven (min. 60cm width)

Procedure:

- 25       A 58x10cm steel panel is degreased with xylene and wiped dry. This is suspended horizontally by metal

clips within the extracted spray booth. The Volstatic gun conditions are set at Applied Voltage 60Kv, air pressure 12 lb/in<sup>2</sup>. 40g of sample are inserted into the hopper feed to the gun and the end of the gun barrel  
5 positioned exactly 20cm from the centrepoint of the panel. The gun is steadied and activated until all the powder has been applied across one face of the panel without movement of the gun and the panel is placed in the Stoving Oven for the appropriate cure schedule.

10 Assessment:

As the gun is held static during application the film across the panel represents a cross-section of the powder cloud. By studying the variation of specific properties across the panel any segregation of differing  
15 particle types is measured. The chosen property to be studied depends on the sample constituents; for example, a matting filler which segregates from the powder would cause a variation in the gloss level across the panel.

A quantitative analysis of the extent of separation  
20 is not possible because of differences in film thickness across the panels caused by the static central position of the gun. The film thickness differences may have an underlying influence on the absolute values but can be removed from the overall separation conclusion by  
25 comparison of more than one panel.

In the following Examples the following products were used in the film-forming components:

cross-linking agents:

for polyesters: TGIC PT810 (Ciba-Geigy)

5 for acrylics: dodecadonic acid (Hüls)

flow aids/flow aid masterbatches:

Uralac P3188 (carboxy-functional polyester resin containing 10% w/w of Acronal 4F flow aid) (DSM)

Uralac 2518 (DSM)

10 Modarez III (Protex-France)

catalysts/catalyst masterbatches:

Curazole C17Z M/B (carboxy-functional polyester resin containing 10% w/w of Curazole C17Z imidazole-based catalyst) (Inhouse Masterbatch from M & T

15 Chemicals) proprietary catalyst

Zinc stearate A (Durham Chemicals)

waxes:

Worlee ADD1200 (micronised synthetic wax surface property modifier) (Worlee-Chemie GmbH)

20 Carnauba wax (Industrial Waxes)

AC8A Wax (polyethylene wax) (Allied Chemicals)

Benzoin (degassing agent) (SNIA UK)

Blanc fixe (extender) (Manchem Ltd.)

pigments:

25 Bayferrox 3950 (Bayer)

Red Oxide 130BM (Bayer)

Carbon black BP1300 (Cabot/Tennent Group)



Black pearls 1300 bulk use (Cabot/Tennent Group)

Ti-pure R960 (Du Pont)

Tiona RCL472 (SCM Chemicals)

Heucosin Fast Blue G1737 (Heubach Chemicals)

5 TS100 silica (Aerosil) (Degussa)

Xylene (cleaning solvent) (Shell Chemicals)

#### Example 1

#### Additions of high levels of catalyst

The catalyst triphenylphosphine (TPP) (supplier  
10 M & T Chemicals) supplied in chip form was prepared for  
use by coffee grinding using a Moulinex grinder, sieving  
to <106  $\mu\text{m}$  and jet milling using a Gueso M100 mill,  
micronising air 8 bar, feed air 1.5 bar. The particle  
size distribution of the jet-milled catalyst was 99%  
15 < 7.9  $\mu\text{m}$ , with a mean particle size of 3  $\mu\text{m}$ .

All formulations produced were based on the white  
polyester/TGIC uncatalysed system detailed below:-

	<u>Base Formulation</u>	<u>% by Wt.</u>
	Carboxy-functional polyester (acid value 39-41)	55.31
20	Triglycidylisocyanurate (TGIC)	6.895
	Titanium dioxide pigment	30.00
	Benzoin	0.3
	Flow Aid (Uralac 2518)	7.5
25		<hr/> 100%

The above formulation has a 1:1 stoichiometry.

Three extruded compositions were produced.

- 1) Base formulation (as described).
- 2) Base formulation + 0.2% TPP (by wt. of total composition).
- 5 3) Base formulation + 0.5% TPP (by wt. of total composition).

Manufacture was carried out by extruding each composition using a Buss (RLK46) extruder (set temperature 140°C, screw speed 7), kibbling the extrudate into chip form, 10 grinding the chip using a Moulinex coffee grinder, and finally sieving through a 106  $\mu$ m mesh.

Five agglomerated compositions were produced:-

- 4) Base formulation.
- 5) Base formulation + 0.2% TPP (by wt. of total composition)
- 15 6) Base formulation + 0.5% TPP (by wt. of total composition)
- 7) Base formulation + 1.0% TPP (by wt. of total composition)
- 20 8) Base formulation + 2.0% TPP (by wt. of total composition)

For each agglomerated composition 4 to 8, manufacture of the base formulation was carried out by extruding and kibbling as for composition (1) above, and the chip was 25 then milled using a condux mill, and subsequently jet-milled using a Gueso mill (M100) with a micronising air

setting 8 bar and feed air 1-5 bar. The particle size distribution (by weight) of the base formulation was 99% < 16  $\mu\text{m}$ .

Portions of the jet-milled base formulations were dry blend mixed with the indicated portions of jet-milled TPP, and the dry blend mixtures of the powder and catalyst were agglomerated using the hydraulic press agglomeration method described above. The resultant plates of material were ground using a Moulinex coffee grinder and sieved through a 106  $\mu\text{m}$  mesh.

All 8 powder samples were assessed for their gel time at 200°C. The results were as follows:

	<u>% Weight of TPP used</u>	<u>Extruded</u>	<u>Agglomerated</u>
	0	>840 secs	>840 secs
15	0.2	134 secs	157 secs
	0.5	58 secs	94 secs
	1.0	-	66 secs
	2.0	-	37 secs

Those systems with higher than normal levels of catalyst addition (e.g. compositions 7 and 8) showed satisfactory mechanical properties and give the option of faster bake systems. Such levels of catalyst addition were not possible for the extruded compositions.

The extruder used in this experiment was a single screw extruder which was flood fed and temperature was

set at 240°C. Available data shows that the residence time of the material in the extruder ranges from 40 to 125 seconds, with the modal residence time being approximately 55 secs. This data in combination with gel  
5 time data illustrates why high level catalyst systems cannot be extruded without significant pre-reaction occurring in the extruder.

### Example 2

#### Low friction coatings

10 The friction-reducing additive, a wax, Du Pont PFA (Trade Mark) (perfluoroalkoxy) powder 532-5010 having a mean particle size: ~30  $\mu\text{m}$ , with 99% <90  $\mu\text{m}$  was used as supplied.

This material was added to the clear powder coating  
15 system below:

	<u>% by wt.</u>
Carboxy-functional polyester (acid value 32-36)	51.92
TGIC	6.88
Uralac P3188 (Flow aid masterbatch)	10.00
20 Benzoin	0.3
Carnauba Wax	0.3
Catalyst masterbatch (Curazole C172)	0.6
	<hr/>
	100% by wt.

25 Four compositions were tested.

1) Clear formulation (normal particle size).

- 2) Dry blend: clear formulation + 20% (by wt. of total composition) PFA
- 3) Co-extruded: clear formulation + 20% (by wt. of total composition) PFA
- 5 4) Fused agglomerate: clear formulation + 20% (by wt. of total composition) PFA

Composition (1) was manufactured by premixing in a Baker Perkins apparatus for 90 secs; extruding on a Buss (PLK46) extruder (screw speed 12, barrel temp. 140°C (set)); kibbling in a Baker Perkins apparatus; micronising on an ACM3 mill (rotor speed 10900, classifier speed 3600, feed rate 2.5); and finally sieving through a 150  $\mu\text{m}$  mesh. The particle size distribution of the clear formulation after sieving was 99% by weight < 104  $\mu\text{m}$ , with a mean particle size of 32-40  $\mu\text{m}$ .

Composition (2) was prepared by adding the wax to the clear formulation and shaking to mix the components.

In the case of composition (3), the wax was added to the formulation before pre-mixing and co-extruded using the Buss extruder (PLK46) at a set temperature of 140°C and screw speed 8, and the extrudate was micronised by coffee grinding (Moulinex) and sieved through a 106  $\mu\text{m}$  sieve.

In the case of composition (4), the clear component prepared as for composition 1 after sieving was micronised to give a particle distribution of 99% < 10  $\mu\text{m}$

with a mean particle size of 4 to 6 $\mu$ m, and th wax was added to the clear component by solvent agglomeration using 22g of methanol added over 6 mins, and a speed of approximately 300 rpm. During the addition of methanol  
5 (BDH Analar), dry compressed air was passed over the sample at approximately 1 litre/min, and after the addition dry compressed air was passed at 15 litres/min for 15 mins. Then the sample was dried for a further 10 mins. before spraying.

10 After drying, the sample was free-flowing and fluidisable, and suitable for electrostatic spraying (only 11% < 10  $\mu$ m). The particle size distribution (by weight) was 99% < 87  $\mu$ m with a mean particle size 28-37 $\mu$ m.

All compositions were applied using standard powder  
15 electrostatic spray apparatus (applied voltage 70Kv). The substrate was degreased untreated cold rolled steel (gauge 1mm) panels of approximately 4" x 22". Stoving was for 15 mins at 200°C (total stoving time).

The coefficient of sliding friction was measured  
20 using the Ministry of Defence test method DEF STAN 80-73/1 for non-slip deck coatings, using the rubber surface and measuring the coefficient only on the dry surface. The coefficient of friction of composition 4 was found to be half that of composition 1, showing that addition of  
25 PFA powder by the agglomeration method described successfully reduced the co-efficient of sliding friction in the

finished film.

Some reduction in coefficient of sliding friction was also obtained with compositions 2 and 3 (i.e. by dry-blend and extrusion methods).

5 Example 3

Incorporation of rubber tougheners

A rubber toughener (Paraloid KH3345 (Trade Mark), ex Rohm & Haas), supplied particle size 98% < 170  $\mu\text{m}$  and mean particle size 90-104  $\mu\text{m}$  was sieved through a 32  $\mu\text{m}$  mesh to give a particle size 94% < 37  $\mu\text{m}$  and mean particle size 21-28  $\mu\text{m}$ .

The rubber toughener was added to a clear polyester/TGIC system with the following formulation:-

	<u>% by wt.</u>
15 Carboxy-functional polyester resin (acid value 35)	91.7
TGIC	6.9
Benzoin	0.4
Flow Agent	1.0
20	<hr/> 100%

Three compositions were manufactured:-

- 1) Clear formulation (as described above).
- 2) Co-extruded composition: clear formulation + 15% (by weight of total composition) rubber toughener.
- 25 3) Fused agglomerate: clear formulation + 15% (by weight of total composition) rubber toughener .

Compositions (1) and (2) were manufactured by extruding on a Buss (PLK46) extruder at temperature 140°C and screw speed 7, kibbling the extrudate into chip form, grinding the chip using a Moulinex coffee grinder, and  
5 sieving through a 106 µm mesh.

In the case of composition (3), the clear component was manufactured by the extrusion, kibbling and grinding steps described above, and then jet milled using a Gueso jet mill M100 with micronising air set at 8 bar and feed  
10 air set at 1.5 bar. The rubber toughener was added to the jet-milled powder and this sample was agglomerated by a solvent agglomeration method, 15 g of methanol (Analar ex. BDH) being used with 100g of jet-milled powder/rubber toughener.

15 All three compositions were applied using standard powder electrostatic spray apparatus (applied voltage 70Kv) to a Bonderite 711 Aluminium (1mm) 6"x4" (ex Brent) substrate. All panels were stoved for 15 mins. at 200°C (total stoving time).

20 The Gardener weight impact tester with a falling 1 kg weight was used to assess the impact resistance of all three formulations.

1 joule forward and reverse impacts on all three compositions showed a degree of cracking or crazing. The  
25 appearance of the rubber toughened and untoughened panels after impact was markedly different.



With composition (1) (no rubber toughener):

Forward Impact (impact directly onto coating surface):

The failure consisted of a series of continuous concentric circles throughout impact.

5 Reverse Impact (impact onto uncoated side of panel):

The failure consisted of continuous radial lines of failure covering the whole impact area.

With compositions 2 and 3 (15% rubber toughener extruded and agglomerated respectively):

10 Reverse Impact:

Impact resulted in discontinuous cracking with a degree of stress whitening which did not cover the whole impact area.

Forward Impact:

15 Impact resulted in short lines of failure encircling the impact area. Unlike composition (1), these lines of failure did not form continuous concentric circles.

It was demonstrated that addition of rubber  
20 toughener caused the nature of the impact failure to change: the rubber toughener reduced the extent of cracking and the lengths of the cracks.

Example 4Gloss reduction by incorporation of an incompatible resin component(a) First example

5	<u>Component A (white, polyester)</u>	<u>% by Wt.</u>
	Carboxy-functional polyester (acid value 29)	45.65
	Uralac P3188 flow aid master batch	7.34
	TGIC	3.42
	Pigment: Ti-Pure R960	15.84
10	Pigment: Tiona RCL472	10.56
	Ac8A Wax	0.20
	Benzoin	0.50
	ADD.1200 Wax	0.50
	Catalyst (zinc stearate A)	0.12
15	Filler (Blanc Fixe)	15.87
	<u>Component B (clear, acrylic)</u>	<u>% by Wt.</u>
	Glycidyl-functional polyacrylate	82.00
	Dodecanedioic acid	16.70
	Benzoin	0.30
20	Flow aid (Modarez III)	1.00

The pre-mixes A and B were each extruded on a Buss PLK46 extruder, screw speed 80 rpm, temperature setting 140°C. The extrudates were then micronised on a Kek mill

and sieved through a 106  $\mu\text{m}$  steel mesh sieve. Both materials were then jet-milled using a Gueso M100 machine operating at the following set conditions: air supply 9 bar, micronising air supply 9 bar, feed air supply 1 bar, 5 material feed rate 70. The particle size distributions obtained were as follows:-

Component A (Polyester)99% below 25  $\mu\text{m}$ mean 6  $\mu\text{m}$ Component B (Acrylic)99% below 25  $\mu\text{m}$ mean 3  $\mu\text{m}$ 

10 For comparison a powder was also prepared by co-extruding the components A and B in a 85/15 ratio and using otherwise identical procedures.

Components A and B were agglomerated in the ratios 90/10 and 85/15 w/w by the hydraulic press method described above. This produced free-flowing and fluidisable 15 powders with a particle size distribution 90% below 120  $\mu\text{m}$  and means of 30-35  $\mu\text{m}$ , with no more than 10% below 10  $\mu\text{m}$ .

The agglomerated powders were applied by standard 20 electrostatic application techniques using 70 Kv applied voltage and stoved for a total of 15 minutes at 200°C in an electric box oven on a 6'x4'x1 mm chromate pretreated aluminium panel (Ardrox Pyrene - Bonderite 711) substrate.

Assessment of the cured films (of ~ 50  $\mu$ m dry film thickness) for gloss, impact resistance and flexibility on the T bend test gave the following results:-

Gloss (recorded at 20°, 60° and 86°C using a Labor

5 Reflektometer)

	<u>90/10 Agglomerate</u>	<u>85/15 Agglomerate</u>	<u>85/15 Extrudate</u>
20°	4%	2%	31%
60°	10%	6%	77%
86°	16%	8%	93%

10 Mechanicals

	<u>90/10 Agglomerate</u>	<u>85/15 Agglomerate</u>	<u>85/15 Extrudate</u>
Impact R	5 J	2.5 J	2.5 J
Flexibility	1 T	2 T	-

- 15 The figures for impact resistance should be compared with figures for the single component systems which are generally 1 J or less for the acrylic and 10 J or greater for the polyester. The results in the T bend test for flexibility show good results with the 85/15 agglomerate
- 20 and very good results for the 90/10 agglomerate.

A segregation test was carried out on the 85/15 agglomerated composition and on a 85/15 dry blend composi-

tion ('normal' particle size distribution) according to the electrostatic separation method described above.

The 60° gloss showed an even 6% test result across the panel sprayed with agglomerated material, while a spread of  
5 between 7 and 30% was obtained for the dry blend material. This demonstrated that no segregation occurred in the agglomerated material, whereas the dry blend separated to some extent on spraying, giving areas rich in either  
10 material and therefore gloss variation across the sprayed panel.

(b) Second Example

Component A was a standard white gloss polyester cross-linked with TGIC.

Component B was jet-milled acrylic powder produced as  
15 described below.

	<u>Composition</u>	<u>Weight (kg)</u>
	Methyl methacrylate	1.20
	Glycidyl methacrylate	0.50
	2-ethyl hexylacrylate	0.30
20	Triganox 21 (peroxide initiator)	0.03
	Xylol	2.00

The xylol was heated to reflux and the methacrylate and hexylacrylate materials and 0.025 kg of Triganox initiator were added over a period of two hours while refluxing.

25 Refluxing was continued for a further one hour, and a further 0.005 kg of triganox initiator were then added, and refluxing was continued for another hour. The solvent was distilled off and any remaining was then vacuum stripped

from the product at below 180°C. The product had viscosity 140 Poise (ICI cone and plate) at 200°C, equivalent weight 568, number average molecular weight 9900 and weight average molecular weight 24000.

5 **Acrylic powder manufacture:**

The acrylic powder was incorporated into a simple powder coating formulation according to the proportions shown below.

		<u>% by wt.</u>
10	Acrylic polymer	73
	Dodecanoic acid	15
	Flow aid (Modarez III)	1
	Benzoin	1
	Filler (Blanc fixe)	10

- 15 The above formulation was mixed in a high intensity mixer and extruded on an MPC30 twin screw extruder. (The set temperature was 125°C, screw speed 400 rpm, torque 60%, feed rate 250). The resultant chip was milled (condux mill) and sieved through a 250 micron mesh. This
- 20 powder was further size-reduced using a Gueso M100 jet mill (micronising air 9 bar, feed air 1 bar).

- A Henschel mixer, modified to incorporate a heating jacket, a cooling jacket, scraper blades for the internal wall and inside of the lid, and an air swept bearing for
- 25 the main rotor, was used for agglomeration.

The agglomeration as carried out as follows: the temperature was set at 72°C, the mixer speed at 2000 rpm for the first minute and then 800 rpm for the remainder of

the process. The machine was charged with 2kg of a 95:5 mix of polyester:acrylic powder. The run time was 30 minutes.

Particle sizes of the starting materials (separately and mixed) and the finished product were determined using a Galai CIS-1 particle sizer. These are presented as evidence of agglomeration.

Size, $\mu\text{m}$	Polyester Powder	Acrylic Powder	Mixture (95:5)	Finished Product
Mean	56.0	4.7	4.4	62.5
% Vol. $<5\mu\text{m}$	0.56	63.9	3.4	0.75
% Vol. $<10\mu\text{m}$	1.93	99.1	7.9	1.6

A sprayed and cured panel had the following gloss measurements:-

At observation angle	20°	60°	85°
gloss (%) finished product	2%	5	4

The reduction of  $< 5\mu\text{m}$  and  $< 10\mu\text{m}$  fractions in the Henschel process are good evidence for agglomeration. The excellent matting effect of the acrylic is shown by the gloss measurements. Whereas the finished product sprayed normally during application, the dry mixture behaved as a cohesive powder (clumping, spitting from the gun, uneven

powder cloud density).

#### Example 5

#### Production of speckled finishes

An agglomerate was prepared from two coloured polyester/TGIC powders (a blue and a white), the white powder having the composition of component A described in Example 4, and the blue powder being composed as follows:

	<u>% by Wt.</u>
Carboxy-functional polyester (acid value 29)	27.70
10 TGIC	4.50
Carboxy-functional polyester (acid value 30-37)	22.16
Uralac P3188 flow aid masterbatch	11.08
Aca8 Wax	0.30
Benzoin	0.20
15 Pigment: RTC30 (TiO <sub>2</sub> pigment)	0.82
Pigment: Heucosin Fast Blue G1737	22.16
Filler (Blanc Fixe)	11.08

The pre-mixes for the blue and white powders were each separately extruded on a Buss PLK46 extruder at a temperature setting of 140°C and screw speed 9. The resulting extrudates were kibbled and micronised by a Kek mill and sieved through 106 µm mesh to give in each case a mean particle size of 30-35 µm and distribution of 99% <120 µm and no more than 10% <10 µm.

25 The two powders were combined in a ratio of 1:1 by



weight by the hydraulic press method described above. A free-flowing and fluidisable powder of mean particle size of 30-35  $\mu\text{m}$  with distribution of 90% <120  $\mu\text{m}$  and no more than 10% <10  $\mu\text{m}$  was produced.

5       The powder was applied by normal electrostatic spray methods and stoved for 15 minutes at 200°C on aluminium Bonderite 711 panels. The films produced had a uniform heterogeneity in colour, i.e. the degree of speckling was constant across the panel; this was measurable by the  
10   Cielab Colour Computer. The flow and levelling and gloss levels remained unchanged as compared with single-coloured panels.

A segregation test was conducted by the electrostatic separation method described above. By colour measurement  
15   across the width of the panel any segregation can be witnessed. A dry-blended mixture of the same coloured particles resulted in considerable segregation across the panel, whereas the agglomerated mixture of the same particles showed no significant segregation.

20   Example 6

(a)   First example

Colour correction

Three colour components ("colour bases") were prepared using the following pigments

- 1) Bayferrox 3950 Yellow Iron Oxide
- 2) Synthetic Micronised Red Oxide Grade 130BM
- 3) Carbon Black High Colour B.P.1300 Type

1)	<u>Bayferrox 3950 Base</u>	<u>% by wt.</u>
5	Carboxy-functional polyester (acid value 32-36)	66.58
	TGIC	5.73
	Uralac P3188 flow aid masterbatch	10.00
	Carnauba Wax	0.30
	Catalyst Masterbatch (Curazole C17Z)	0.30
10	Bayferrox 3950 pigment	6.48
	Filler (Blanc Fixe)	10.00

Extrusion was carried out in a Buss PLK46 extruder at a temperature setting of 140°C and screw speed 9; micronising was carried out by a Kek mill apparatus. After jet-

15 milling using a Gueso M100 apparatus under a feed air pressure of 0.5 bar, a feed rate of 70 and a micronising air pressure of 8-10 bar, the powder product had a particle size distribution of 99% <8 µm and a mean particle size of 3.4 µm.

20	2) <u>Synthetic Micronised Red Oxide</u>	
	<u>130 BM Base</u>	<u>% by wt.</u>
	Carboxy-functional polyester (acid value 32-36)	71.88
	TGIC	6.13
	Uralac P3188	10.00
25	Carnauba Wax	0.30
	Benzoin	0.30

Catalyst (Curazole C17Z) Masterbatch	0.60
Red Oxide 130BM pigment	5.79
Filler (Blanc Fixe)	5.00

Manufacture was identical to that described for the  
5 Bayferrox 3950 base (1) above. The produced powder had a particle size distribution of 99% <8  $\mu\text{m}$  and a mean particle size of 3.9  $\mu\text{m}$ .

3) Carbon Black High Colour

	<u>BP1300 Type Base</u>	<u>% by wt.</u>
10	Carboxy-functional polyester (acid value 32-36)	67.88
	TGIC	5.83
	Uralac P3188	10.00
	Carnauba Wax	0.30
	Benzoin	0.30
15	Catalyst Masterbatch (Curazole C17Z)	0.60
	Carbon Black BP1300 pigment	3.09
	Filler (Blanc Fixe)	12.00

Manufacture was as described in (1) above, except that  
a screw speed 8 was used in extrusion. The produced powder  
20 had a particle size distribution of 99% <8  $\mu\text{m}$  and a mean particle of 3.5  $\mu\text{m}$ .

The colour bases were then added to a conventionally-sized powder coating composition which was slightly off-shade from the desired colour. Calculations using a  
25 colour computer gave the amounts of each of the pigments required to achieve colour correction.

Agglomeration was carried out by the hydraulic press method described above. The resultant free-flowing and fluidisable powder had a particle size distribution of 90% < 120  $\mu\text{m}$  and no more than 10% < 10  $\mu\text{m}$ .

- 5        For comparison purposes, the three pigments were used also in a dry pigment addition technique.

The agglomerate was applied by normal electrostatic spray methods and stoved for 15 minutes at 200°C on aluminium Bonderite 711 panels.

- 10       Both correction additive types lead to the colour meeting the specification. The colour bases addition, however, gave a more accurate correction than the dry pigments addition. Close inspection (<15cm) of the dry pigment-corrected film showed a degree of inhomogeneity  
15 where areas of varying colours could be just distinguished with the naked eye. This was not seen in the colour base correction. There was no significant variation in flow and levelling caused by increased solids:binder ratio of the films.

- 20    (b) Second example

#### Manufacture of components:

A polyester powder of normal particle size distribution was produced by standard methods.

A second polyester component was produced as follows:

	<u>% by wt.</u>
Polyester polymer	76.15
Triglycidyl isocyanurate (TGIC)	5.7
Scarlet chrome sicomin red pigment	16.5
5 Benzoin	0.3
Acrylate flow aid	1.0
Catalyst	0.05

The ingredients were mixed in a high intensity mixer prior to extrusion through a BUSS PR46 Kno-Kneader extruder set  
10 at a barrel temperature of 140°C and screw speed of 8.

The chip was ground and sieved to below 250µm before being micronised to 90% by vol. < 10µm particle size in a Gueso M.100 jet-mill (micronising air pressure between 8-10 bar, feed air pressure = 1 bar and powder feed rating = 70).

15 **Agglomeration conditions:**

2kg of a 95:5 by weight mix of normal particle size distribution white polyester : jet-milled orange polyester powder was charged into the modified Henschel apparatus of Example 4b. Conditions in the apparatus were Jacket  
20 Temperature Setting of 65-68°C and speed of 1500 rpm for 55 minutes. The mixer speed was adjusted to 1600 rpm and the Temperature Setting increased to 70°C for a further 20 minutes.

**Evidence of agglomeration:**

25 Panels were sprayed using a stationary electrostatic powder gun aimed at the centre of a panel. The stoved

films should therefore display any separation of the powders due to non-agglomeration by way of the film colour differences at different positions on the panel. Colour computer measurements (ICS Colour Systems Micromatch 9000) were taken on the films at positions that were at the centre of the panel and at a set distance below this (125mm).

The variance in colour between the centre position and the set position in the non-agglomerated starting mixture was compared to the variance in the agglomerated product using the same technique.

	<u><math>\Delta E</math></u>
Starting material	4.69
Product	0.94

$E$  is a measure of the variance in colour space position between two points and is calculated from:

$$\Delta E = \Delta L + \Delta A + \Delta B$$

where  $\Delta L$  = variance in luminance axis,  
i.e. darker/lighter  
where  $\Delta A$  = variance in green/red axis  
where  $\Delta B$  = variance in blue/yellow axis.

Therefore the lower the value of  $\Delta E$  the closer the colour is between the positions.

Particle size analyses of the starting materials and the finished product were conducted using a Galai CIS-1 particle analyser.

	Size ( $\mu\text{m}$ )	Whit Polyester	Orange Polyester	95:5 Mix	Agglomerated Product
	Mean	56.0	3.5	52.1	60.6
5	% vol <5	0.6	84.0	2.7	0.4
	% vol <10	1.9	100.0	4.9	1.3

The reduction in <5 $\mu\text{m}$  and <10 $\mu\text{m}$  fractions indicate that such particles have been consumed in agglomeration, and the marginal increase in mean particle size is further evidence of fusion of the large white particles with the much finer tinting powder.

This resulted in a film of a colour that has been tinted away from the colour of the normal particle size base powder.

#### 15 Example 7

##### Abrasion-resistant coating

Calcined bauxite (300 mesh) FQ0060, an aluminium oxide with up to 12% SiO<sub>2</sub> supplied by C.E. Ramsden, with particle size 99% below 30  $\mu\text{m}$ , mean size 5.8  $\mu\text{m}$  was used as

20 additive.

##### Film-forming component

##### % by Wt.

	Carboxy-functional polyester (acid value 29)	54.67
	Uralac P3188	10.93
	TGIC	4.86
25	ACA8 wax	0.30
	Benzoin	0.20
	Pigment: Black pearls 1300 bulk use	1.70

Filler (Blanc Fixe) 27.34

Addition prior to milling:-

Dry flow additive (silica agent TS100) 0.50

The raw materials for the film-forming component were  
5 extruded on a Buss PLK46 laboratory extruder (temperature  
set at 140°C, screw speed setting 9) and after addition of  
the silica agent micronised in a Kek mill and subsequently  
jet-milled using a Gueso M100 machine (feed air pressure 1  
bar, micronising pressure 9 bar, feed rate 70) to give a  
10 particle size 99% below 20  $\mu\text{m}$ , with mean size 4.5  $\mu\text{m}$ .

Bauxite was added to the powder at 25% by weight and  
then processed by the hydraulic press method. The product  
was a free-flowing and fluidisable powder, particle size  
~ 90% below 120  $\mu\text{m}$ , 10% below 10  $\mu\text{m}$ , mean size 30-35  $\mu\text{m}$ .

15 The agglomerated powder and the film-forming component  
were each applied by a standard electrostatic spraying  
method (applied voltage 70Kv), to a Taber panel, cold  
rolled steel plate 4" square with 1/4" hole centrally  
located, 0.04" (1mm) thick. After 15 minutes stoving at  
20 200°C, the abrasion resistance of the panels was determined  
by the standard test method for Abrasion Resistance of  
Organic Coatings by the Taber Abrader as described in ASTM  
D4060-84. The following test details were noted:-

Room temperature 20°C

25 Coating thickness approximately 60  $\mu\text{m}$

Calibrase CS-10 abrasive wheels



1000g applied load

1000 wear cycles

The weight loss for the panel coated in film-forming powder (standard panel) and for the panel coated in agglomerate

5 (test panel) were as follows:

Weight loss for standard panel = 0.050 g

Weight loss for test panel = 0.021 g

This shows that the test panel coated with the agglomerate was more significantly resistant to abrasion than the

10 standard panel.

#### Example 8

##### Non-slip powder coating

Sand with a particle size 99% below 180  $\mu\text{m}$ , mean size 120  $\mu\text{m}$ , was dried in an oven, Kek milled and sieved through  
15 150  $\mu\text{m}$  mesh, then re-sieved through 106  $\mu\text{m}$  mesh and added in a 1:1 weight ratio to the powdered film-forming component of Example 7.

The components were agglomerated by the hydraulic press method, although the powder was sieved through a  
20 150  $\mu\text{m}$  mesh instead of 106  $\mu\text{m}$  mesh as indicated. The product was a free-flowing and fluidisable powder, particle size  $\sim$  99% below 180  $\mu\text{m}$ , 10% below 10  $\mu\text{m}$ , mean size 75  $\mu\text{m}$ .

The agglomerated product and binder were each applied by standard electrostatic spraying method (applied voltage  
25 70Kv) to gradient panels, cold rolled steel 565mm x 100mm

x 1mm thick and stoved for 15 minutes at 200°C.

Non-slip properties were measured by a Ministry of Defence Standard test for non-slip deck coatings - DEF STAN 80/73-1 (see Example 2). Tests were carried out on a  
5 gradient panel coated with the film-forming component alone (standard panel) and a panel coated with the agglomerated sample. The "non-slip" panel could then be compared with the standard panel to determine the differences in the coefficient of static friction and the coefficient of  
10 sliding friction.

An applied load of 5.7Kgs was used in these tests. The same values were obtained for the coefficient of static friction as for the coefficient of sliding friction, as follows:-

15 "Standard" Panel = 0.48

"Non-Slip" Panel = 0.96

Clearly the "non-slip" panel offers a greater resistance to slip than the "standard" panel.

A segregation test was carried out by the electro-  
20 static separation method. Both the "agglomerated" panel and the "dry blended" panel were inspected visually. The sand on the "agglomerated" panel was totally encapsulated by the powder coating and had adhered to the substrate, whereas the sand on the "dry blended" panel had gathered at  
25 both ends of the panel and could be brushed off. This showed that segregation had occurred in the "dry blended" panel.

Example 9Addition of Syenex extender

(Syenex is a Trade Mark)

Experimental work has shown that wear rates on  
5 extruders processing formulations including very hard  
materials such as Syenex extenders are approximately twice  
that compared to similar particle size  $\text{CaCO}_3$  and  $\text{BaSO}_4$   
extenders. Their use in the agglomeration process (thus  
avoiding extruder wear) was tested as follows:

10 Syenex, supplied by Elkem Nefelin in various grades as  
follows:

Syenex 10 - 99% below 8  $\mu\text{m}$ , mean size 2.7  $\mu\text{m}$

Syenex 20 - 99% below 20  $\mu\text{m}$ , mean size 5  $\mu\text{m}$

Syenex 30 - 99% below 30  $\mu\text{m}$ , mean size 7.5  $\mu\text{m}$

15 Syenex 40 - 99% below 44  $\mu\text{m}$ , mean size 10  $\mu\text{m}$

was added to the powdered film-forming component of Example  
7 at 5% by weight and agglomerated by the hydraulic press  
method. The product was a free-flowing and fluidisable  
powder, having a particle size of 90% below 120  $\mu\text{m}$ , with  
20 10% below 10  $\mu\text{m}$ , and a mean size of 30-35  $\mu\text{m}$ .

The agglomerate was applied by the standard electro-  
static spraying method (applied voltage 70Kv) to Bonderite  
B711 Aluminium panels for normal use and to gradient  
panels, cold rolled steel 565mm x 100mm x 1mm thick for the

segregation test. All panels were stoved for 15 minutes at 200°C. Gloss levels were recorded at 20° and 60° using a Labor Reflektometer. Comparison of a panel coated with the standard powder (the binder component alone) with one  
5 coated with agglomerated powder showed that Syenex reduced gloss levels, although not very greatly; the coarser the grade of Syenex the more the gloss level was reduced. Comparison of the gloss levels of "extruded" and "agglomerated" panels containing the same grade and amount  
10 of Syenex was also made; the "agglomerated" panels produced a slightly larger reduction in gloss level.

The effect of agglomeration on segregation was also tested. The "agglomerated" panel was measured for gloss level using a Labor Reflektometer in five different places  
15 and values recorded at 20° and 60°. Measurements were taken at the centre of the test panel, 3" from the centre in both directions and 6" from the centre in both directions. The same procedure was repeated for a dry-blended panel. Results showed the agglomerated panel to have  
20 fairly constant readings along its length, whereas the dry blended panel gave widely differing readings along its length, suggesting that separation occurred in the dry blended panel.

Example 10Textured finishes in films by addition of a thermoplastic texturing agent

The texturing agent - cellulose acetate butyrate 551-  
5 0.2 (CAB) supplied by Eggar Chemicals as powder, with a  
particle size distribution 100% under 188  $\mu\text{m}$ , 5% under  
10  $\mu\text{m}$ , and a mean of 96  $\mu\text{m}$ , was used as additive.

The film-forming component had the composition of the  
binder component in Example 7, but was prepared by extrud-  
10 ing on a Buss PLK46 extruder, at screw speed 80 rpm and set  
temperature 140°C, micronising using a Kek mill, sieving  
using 106  $\mu\text{m}$  steel mesh hand sieve, and then jet-milled  
using a Gueso M100 machine with the following set condi-  
tions: feed air pressure 1 bar, micronising air pressure 9  
15 bar, feed rate 70. This gave a product with a particle  
size 99% below 25  $\mu\text{m}$  and mean 4.5  $\mu\text{m}$ .

This powder was then agglomerated with 0.2% CAB using  
the standard hydraulic press method described above to give  
a free-flowing and fluidisable powder with a particle size  
20 99% below 120  $\mu\text{m}$ , mean 30-35  $\mu\text{m}$ , and no more than 10% below  
10  $\mu\text{m}$ . This material was suitable for application by  
standard electrostatic application techniques using an  
applied voltage of 70 Kv.

Cured films of 50  $\mu\text{m}$  dry film thickness were prepared  
25 by spraying onto 6'x4'x1mm chromate pretreated aluminium  
panels, Bonderite 711 (Ardrox Pyrene) and stoving for 15

minutes at 200°C total oven time (conventional box oven).

Visual inspection indicates that the agglomerated product gives rise to a textured effect, though this is not as pronounced as for the conventionally prepared material of the same composition. However CAB is not expected to segregate from the agglomerated product on application, whereas it does from conventionally prepared products.

#### Example 11

##### Addition of a tribocharging additive

10 First component: a polyester gloss powder coating was manufactured using the following formulation:

	<u>% wt.</u>
Polyester polymer	68.1
TGIC	4.6
15 Titanium dioxide	24.9
Other pigments	0.6
Flow agent	1.3
Benzoin	0.3
Wax	0.2

20 A powder of conventional particle size was prepared.

Second component: tribocharging additive jet-milled (77% < 1µm, 99% < 4µm by number). This component was added to the first component in an amount of 1% by weight, based on the weight of the total mixture.

25 The agglomeration of the tribo agent onto the powder particles was achieved using the Henschel equipment

described in Example 4(b). The agglomeration conditions were as follows: temperature at 65°C, mixer speed at 2100 rpm, with 2.4kg of powder containing 1% of tribo additive being added to the mixer. The Henschel apparatus  
5 was then run at this speed for 15 minutes, after which time the powder was quickly removed from the vessel and cooled. This sample was now ready for testing on the tribo equipment.

Other reference specimens were also prepared to test  
10 how agglomerations of this type performed in terms of its ease of friction charging with respect to identical compositions that had not undergone the same mechanical treatment. These reference samples were as follows:

1) 99% polyester powder plus 1% tribo additive added  
15 at the post-milled stage, mixed by simple vigorous shaking together in a plastic bag (thus the tribo additive was a free component).

2) 99% polyester powder plus 1% tribo additive which had been masterbatched in the polyester resin (200°C for 30  
20 minutes under nitrogen) prior to the preparation of the sample.

3) 99% polyester powder plus 1% tribo additive which was included in the formulation and added prior to the extrusion stage, though this would not have melted at any  
25 point in the processing, unlike the masterbatched material (extrusion takes place at typically 120°C).

4) 100% polyester powder, a control sample.

Testing for tribocharging characteristics was carried out by measuring the charge to mass ratio of each sample on passing through a Nordsen ICAB gun. The powder sample was fed from a fluidised bed through a length of PVC tubing to the inlet of the gun at an approximate rate of 100g/minute. Both the air pressure inside the bed and that passing into the gun was set at a constant 2 bar. Once the powder had been passed through the gun, it was separated from the air stream using a standard cyclone, which also acts to discharge fully the powder, and the build-up of electrostatic charge on the cyclone was measured and used to gauge the tribo-charging that occurred as it passed through the gun. After collection of the powder once it had been separated from the air, its mass over a known period of time was measured and a charge to mass ratio for that particular sample calculated. The sample was then returned to the fluidised bed and another run was taken. Each powder was tested a number of times until the calculated charge to mass ratios were found to stabilise well within the experimental errors of the operation which were around 5%.

The charge to mass data collected on the various powder specimens tested on the tribo equipment is displayed in Figure 10. It can be seen that the pure polyester powder charged significantly less than any of the other samples since the additive itself enhanced the ability of



the polyester to friction charge, irrespective of the way in which it was added to the powder. Moreover, from the quite dramatic reduction in charging from reference sample (1) with run number, loss of the additive must occur  
5 during recycling, even when a highly efficient technique of recovery is employed.

Both the masterbatched and extruded samples were found to display enhanced tribo activity, but to a level which under normal circumstances would not be sufficient for  
10 satisfactory adhesion of the powder to a metallic substrate. This result appears to support the hypothesis that charge transfer is a surface phenomenon, as the charging of these samples is less than the free additive powder since much of the additive in these cases is trapped inside the  
15 particles.

The most significant improvement in the tribo characteristics of any of the samples prepared was, however, found in the agglomerated powder. This powder displayed two important characteristics; firstly, it showed a quite  
20 significant increase in its ability to tribo-charge (roughly equal to that of reference sample (1) initially), indicating that the additive was working effectively and, secondly, its magnitude of charging did not appear to diminish with run number as with reference sample (1).  
25 This second point is of great significance since it shows that the small additive particles had become physically bonded to the polyester powder and, as a result, loss of

this agent during recycling occurs only at roughly the same rate as loss of the powder itself.

Example 12

Surface segregation (stratification)

5        **First component:** A standard high gloss white polyester was slightly reduced in size by sieving using a 53 $\mu$ m sieve to give 90% by volume < 53 $\mu$ m.

**Second component:** A glycidyl-functional acrylic polymer, having equivalent weight 570, viscosity 140 Poise  
10    (200°C, ICI Cone and Plate), number average molecular weight 9900 and weight average molecular weight 24000, was granulated to chip size 3-5mm and premixed with other ingredients of the formulation given below before extrusion using a Buss Ko-kneader, with barrel temperature set at 75  
15    to 85°C.

	% by wt.
Acrylic polymer	47.5
Dodecanoic acid	11.1
Flow aid (Modarez)	1.0
20    Filler (Blanc fixe)	39.0
Violet pigment	1.0
Benzoin	0.4

The extrudate was cooled and ground, then sieved to 90% by volume < 53 $\mu$ m.

25        The polyester and acrylic powders were combined in

80:20 proportions by weight and premixed using a small Moulinex mixer (product I). The composition was agglomerated into a pellet using a Moore's press (hydraulic press method described above) at 100°C for 30  
5 seconds. The pellet (product II) was broken into chip, ground and sieved through 106µm mesh to yield product III.

For comparison purposes, a mixture of polyester and acrylic powders, identical to that described above, was combined by re-extrusion using a Buss Ko-kneader at 90°C.  
10 Powder was obtained from the extrudate as described above (product IV).

Resistance to segregation on application was tested using the standard test described above where powder is sprayed through a stationary gun onto a horizontally  
15 positioned panel. Panels were stoved at 180°C for 10 minutes. Colour measurements were made at the centre and 20 cm from the centre of the panel (in a horizontal direction). Since the acrylic powder is violet and the polyester is white, colour measurement gave an indication  
20 of the composition on the panel, and colour difference across the panel can be used as a measure of segregation.

In contrast to the agglomerated powder III, the mixture of the polyester and acrylic powder (product I) showed a marked tendency to segregate during application,  
25 the polyester preferentially depositing on the centre of the panel and the acrylic tending to deposit away from the

centre.

Colour difference

	<u><math>\Delta E</math></u>
5 Product I	35.2
Product III	0.6

This clearly demonstrates that agglomeration of the two components prevents segregation during application.

The extent of surface segregation (stratification) was  
 10 tested by colour measurements using a Cielab Colour  
 Computer (10° observer D65 illuminant). The individual  
 components and powders III and IV above were applied to a  
 panel and stoved at 180°C for 10 minutes before colour  
 measurement. For product II the flat pressed pellet (that  
 15 has not been subjected to a stoving treatment) was used;  
 this represents the closest approximation to the colour  
 generated by mixing the specified proportions of white and  
 violet).

	L	a	b
20 White polyester	94.8	-1.1	1.52
Violet acrylic	28.5	13.6	-21.2
Product II	67.4	13.3	-25.6
Product III	54.6	23.9	-35.3
Product IV	65.1	16.0	-28.4

25 III gave a very much deeper shade than IV, and IV deeper

than III.

Comparison of the colour of Product III with that of product II indicates that the acrylic component tended to migrate to the surface during film formation. Comparison  
5 of product III with product IV indicates that the migration was much more efficient where the product was manufactured by an agglomeration route, as opposed to co-extrusion of the polyester and acrylic components.

The Example provides confirmation for our view that  
10 surface segregation is promoted by having the separating components as discrete domains of substantial size before film-formation begins; in contrast surface segregation is severely retarded when components are intimately blended.

In the above Examples the Buss extruder speed settings  
15 correspond to the following actual screw speeds

setting 7 - 75 rpm

8 - 85 rpm

9 - 93 rpm

The feeder for the Gueso M100 jet-mill was an ACCURATGE  
20 feeder 310 Model supplied by March Systems Limited.

The above Examples are summarised in the following Table.

TABLE

Example	Size 1st film-forming comp.	Additive	Proportion of additive by wt.	Size of additive	Result	Agglomerate type
1	d	catalyst	0.2 to 2%	d	faster gelling	III
2	d	PTE-type	20%	99% < 90 $\mu$ m mean 30 $\mu$ m (f)	low friction	IIIA
3	d	rubber toughener	15%	b	improved impact resistance	IIIA
4a	d	uncoloured	10%; 15%	d	gloss reduction	III
4b	c	acrylic	5%			I
5	b	differently coloured polyester	50%	b	speckled finish	II
6a	c	"	as required	d	colour tinting/correction	I
6b			5%			
7	d	bauxite	25%	d	abrasion resistance	III
8	d	sand	50%	> 10% $\geq$ 50 $\mu$ m	non-slip coating	IIIA
9	d	extender Syrenex 10,20 Syrenex 30,40	5%	d	cost reduction reduced extruder wear	III
10	d	CAB	0.2%	large - mean 96 $\mu$ m	texture	IIIA
11	c	tribo-charging additive	1%	d	tribo-charging effect retained on recycling	I
12	b	acrylic	20%	b	stratification	II

b =  $\geq 90\%$  by vol. < 50 $\mu$ m, > 10% by vol.  $\geq 20\mu$ m, mean 15-35 $\mu$ m (fluidisable)  
c = > 10% by vol.  $\geq 50\mu$ m, > 90% by vol. < 70 $\mu$ m, < 70% by vol. < 50 $\mu$ m, mean 35-60 $\mu$ m, (fluidisable)  
d =  $\geq 90\%$  by vol. < 20 $\mu$ m, mean 1.5-12 $\mu$ m (non-fluidisable)  
(f) = fluidisable (nf) = not fluidisable

CLAIMS

1. A composition suitable for application as a powder coating and which is in the form of a fused agglomerate of different particulate components consisting of a primary film-forming component and one or more other components selected from film-forming and non-film-forming components.

2. A composition suitable for application as a powder coating and which is in the form of a fused agglomerate of different particulate components consisting of a primary film-forming component and one or more other components selected from film-forming and non-film-forming components, provided that,

- if the agglomerate contains a metallic or lustre component and a film-forming component of mean particle size 35 to 60 $\mu$ m and no more than 70% by volume < 50 $\mu$ m, it also contains an incompatible film-forming component or a non-film-forming performance component or two or more such components, and
- if the agglomerate contains two or more differently coloured compatible film-forming components and optionally an uncoloured compatible film-forming component and the size of the particles in each of those film-forming components is sufficiently low that when the powder coating is applied to a

substrate and heated to form a continuous coating the differences in colour in the cured powder coating arising from the different coloured and any uncoloured particles cannot be discerned by the human eye, it also contains an incompatible film-forming component or a non-film-forming component or two or more such components.

3. A composition suitable for application as a powder coating and which is in the form of a fused agglomerate of different particulate components consisting of a primary film-forming component and one or more other components selected from film-forming and non-film-forming components, provided that,

- if the agglomerate contains a metallic or lustre component and a fluidisable film-forming component, it also contains an incompatible film-forming component or a non-film-forming performance component or two or more such components, and
- if the agglomerate contains two or more differently coloured compatible film-forming components and optionally an uncoloured compatible film-forming component and the size of the particles in each of those film-forming components is sufficiently low that when the powder coating is applied to a substrate and heated to form a continuous coating the differences in colour in the cured powder



coating arising from the different coloured and any uncoloured particles cannot be discerned by the human eye, it also contains an incompatible film-forming component or a non-film-forming component or two or more such components.

4. A composition as claimed in any one of claims 1 to 3, which includes a film-forming component incompatible with the primary film-forming component and/or one or more non-film-forming components.

5. A composition as claimed in claim 1, wherein the different components comprise

- A. a primary, coloured or uncoloured, film-forming component, and
- B. (i) a coloured or uncoloured film-forming component incompatible with the primary film-forming component (A), or  
(ii) a non-film-forming performance additive, or two or more of any of such components specified in (i) and (ii)  
and/or  
(iii) - in the case of a primary film-forming component (A) that is coloured, a further differently coloured compatible film-forming component, the particle sizes of these two

components being such that when the composition is applied to a substrate and heated to form a continuous coating the differences in colour in the cured composition arising from the different coloured particles can be discerned by the human eye, or

- (iv) - in the case of a fluidisable primary film-forming component (A) that is coloured, one or more further differently coloured components selected from colouring pigments and film-forming components compatible with the primary film-forming components, each of such a colour and in an amount and of a particle size sufficiently small that when the composition is applied to a substrate and heated to form a continuous coating the differences in colour in the cured composition arising from the different coloured particles cannot be discerned by the human eye.

6. A composition as claimed in any one of claims 1 to 4, wherein the primary film-forming component is coloured and fluidisable and the agglomerate includes one or more differently coloured components selected from colouring pigments and film-forming components compatible with the primary film-forming agent, each of such a

colour and in an amount and of a size sufficiently small that when the composition is applied to a substrate and heated to form a continuous coating the differences in colour in the cured composition arising from the different coloured particles cannot be discerned by the human eye.

7. A composition as claimed in any one of claims 1 to 4, wherein the primary film-forming component is coloured and the agglomerate includes a differently coloured compatible film-forming component, the particle sizes of these components being such that when the composition is applied to a substrate and heated to form a continuous coating the differences in colour in the cured composition arising from the different coloured particles can be discerned by the human eye.

8. A composition as claimed in any one of claims 1 to 7, which includes two or more coloured compatible film-forming components, the particle sizes of each of these components being sufficiently low that when the composition is applied to a substrate and heated to form a continuous coating the differences in colour in the cured composition arising from the different coloured particles cannot be discerned by the human eye.

9. A composition as claimed in any one of claims 1

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to 8, which includes one or more particulate components selected from texturing agents, metallic or mica pigments, colouring pigments and fillers/extenders.

10. A composition as claimed in any one of claims 4 to 9, which includes one or more non-film-forming performance component(s) selected from toughening agents, friction-reducing additives, strengthening agents, microcapsules; zinc; sand, metal carbides, bauxite and other abrasive materials; catalysts; biological material, intumescent pigments, thermochromic pigments, and other heat-sensitive materials; tribocharging additives and corona-charging additives; and water-soluble material.

11. A composition as claimed in any one of claims 1 to 10, which includes a second film-forming component or a non-film-forming component, the identity, amount and particle size of this component and of the principal film-forming component being such that when the powder coating is applied to a substrate and heated to form a continuous coating these components are incompatible and a matting effect is obtained.

12. A composition as claimed in any one of claims 4 to 11, which includes a second film-forming component incompatible with the principal film-forming component,

the identity, amount and particle size of this component and of the principal film-forming component being such that when the powder coating is applied to a substrate and heated to form a continuous coating these two components segregate and form a multilayer system.

13. A composition as claimed in any one of claims 1 to 11, wherein the primary film-forming component is more than 10% by volume  $\geq 50\mu\text{m}$ .

14. A composition as claimed in any one of claims 1 to 12, wherein the primary and/or another film-forming component has a particle size at least 90% by volume  $< 50\mu\text{m}$ .

15. A composition as claimed in claim 14, wherein the primary and/or another film-forming component has a particle size at least 90% by volume  $< 50\mu\text{m}$ , more than 10% by volume  $\geq 20\mu\text{m}$  and a mean particle size in the range of from 15 to  $35\mu\text{m}$ .

16. A composition as claimed in any one of claims 1 to 14, wherein the primary and/or another film-forming component has a particle size at least 90% by volume  $< 20\mu\text{m}$ .

17. A composition as claimed in claim 16, wherein

the particle size of the primary and/or another film-forming component is at least 90% by volume  $< 10\mu\text{m}$ .

18. A composition as claimed in claim 16 or claim 17, wherein the mean particle size of the primary and/or another film-forming component is in the range of from 1.5 to  $12\mu\text{m}$ .

19. A composition as claimed in any one of claims 1 to 6, which comprises

- (i) a film-forming component more than 10% by volume  $\geq 50\mu\text{m}$  and mean particle size in the range of from 25 to  $50\mu\text{m}$ , and
- (ii) a film-forming or non-film-forming component at least 90% by volume  $< 20\mu\text{m}$ , or two or more such components.

20. A composition as claimed in claim 19, wherein component (i) is no more than 70%  $< 50\mu\text{m}$  and has a mean particle size in the range of from 35 to  $50\mu\text{m}$ .

21. A composition as claimed in claim 19 or claim 20, wherein the or each component (ii), independently of the others, has the size specified in any one of claims 16 to 18.

22. A composition as claimed in any one of claims 1

to 5 or claim 8, wherein each component, independently of the others, is of the size specified in any one of claims 16 to 18.

23. A composition as claimed in any one of claims 19 to 22, wherein the non-film-forming component is selected from colouring pigments, fillers/extenders, non-film-forming polymers, heterogeneous catalysts, toughening agents, friction-reducing additives, microcapsules, catalysts, biological material, intumescent pigments, thermochromic pigments, and other heat-sensitive materials, tribocharging additives, corona-charging additives and water-soluble material.

24. A composition as claimed in any one of claims 16 to 18, which includes as larger-sized component an incompatible film-forming component or a cellulose acetate butyrate resin, a metallic or mica pigment, fibres, zinc, microcapsules, a friction-reducing additive, a non-film-forming polymer, a filler/extender of large particle size, or a water-soluble product.

25. A composition as claimed in any one of claims 1 to 5 or claim 7, wherein each component, independently of the others, has the size specified in claim 15.

26. A composition as claimed in claim 25, wherein

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one of the components is a cellulose acetate butyrate resin, a metallic or mica pigment, fibres, zinc, micro-capsules, a friction-reducing additive, a non-film-forming polymer, a filler/extender of large particle size, or a water-soluble product.

27. A composition as claimed in claim 12, which comprises the following incompatible film-forming components:

(i) acrylic, and

(ii) polyester,

or

(i) polyvinylidene difluoride co-extruded with acrylic, and

(ii) epoxy, polyester, polyurethane or polyester co-extruded with epoxy,

or

(i) polyvinylidene difluoride, and

(ii) epoxy,

and wherein the component combinations are as specified in any one of claims 24 to 26.

28. A composition as claimed in claim 27, wherein component (ii) is at least 10% by weight of the total film-forming components.

29. A composition as claimed in claim 27, wherein



component (ii) is from 25 to 50% by weight of the total film-forming components.

30. A composition as claimed in any one of claims 17 to 29, which includes a film-forming component incompatible with the primary film-forming component or a non-film-forming polymeric component for the reduction of gloss.

31. A composition as claimed in claim 30, wherein the gloss-reducing incompatible component has a size as specified in any one of claims 16 to 18.

32. A composition as claimed in claim 30 or claim 31, wherein the gloss-reducing incompatible component is up to 15% of the total film-forming components.

33. A composition as claimed in any one of claims 1 to 32, wherein the mean particle size of the agglomerate is in the range of from 25 to 50 $\mu$ m.

34. A composition as claimed in claim 1, substantially as described in any one of the Examples herein.

35. A process for the preparation of a composition as claimed in any one of claims 1 to 34, characterised by providing a primary film-forming component and one or

more other, different, components selected from film-forming components and non-film-forming components, and mixing and agglomerating the components into fused composite particles such that the composition is air fluidisable and can be applied to a substrate by electrostatic spray.

36. A process for the preparation of a composition as claimed in any one of claims 1 to 34, characterised by providing a primary film-forming component and one or more other, different, components selected from film-forming components and non-film-forming components, and comminuting the or at least one of the film-forming components and if appropriate or required one or more non-film-forming component(s), and mixing and agglomerating the components into composite particles such that the composition is air fluidisable and can be applied to a substrate by electrostatic spray.

37. A process as claimed in claim 35 or claim 36, wherein the mixed particles are agglomerated to produce fused composite particles of mean particle size 15 to 80 $\mu$ m.

38. A process as claimed in claim 37, wherein the mixed particles are agglomerated to produce fused composite particles of mean particle size 25 to 50 $\mu$ m.

39. A process as claimed in any one of claims 35 to 38, wherein the mixing and agglomeration are carried out by a solvent agglomeration process.

40. A process as claimed in any one of claims 35 to 38, wherein the components are mixed as dry powders, and the particles are subjected to mechanical forces sufficient to cause agglomeration of particles by fusion.

41. A process as claimed in claim 35 or claim 36, which is carried out substantially as described herein.

42. A process as claimed in claim 35 or claim 36, which is carried out substantially as described in any one of the Examples herein.

43. A powder coating composition whenever prepared by a process according to any one of claims 35 to 42.

44. Use of an additive selected from film-forming components having a particle size at least 90% by volume  $< 50\mu\text{m}$  and more than 10% by volume  $\geq 20\mu\text{m}$  and a mean particle size in the range of from 15 to  $35\mu\text{m}$ ; toughening agents, friction-reducing additives, strengthening agents, microcapsules; zinc; sand, metal carbides, bauxite and other abrasive materials; catalysts;

biological material, intumescent pigments, thermochromic pigments, and other heat-sensitive materials; tribo-charging additives and corona-charging additives; and water-soluble material, as a separate particulate component in the preparation of a composition in the form of a fused agglomerate of different particulate components for powder coating a substrate.

45. Use of an acrylic film-former as or in a separate particulate component for addition to a particulate polyester, epoxy, polyester-epoxy or polyurethane component in the preparation of a composition in the form of a fused agglomerate of different particulate components for powder coating a substrate.

46. A process for powder coating a substrate, characterised in that a composition according to any one of claims 1 to 34 or claim 43 is applied to the substrate and heated to form a continuous coating.

47. A substrate coated by a process according to claim 46.

48. A composition as claimed in any one of claims 1 to 34 or claim 43, when used in a powder coating process.

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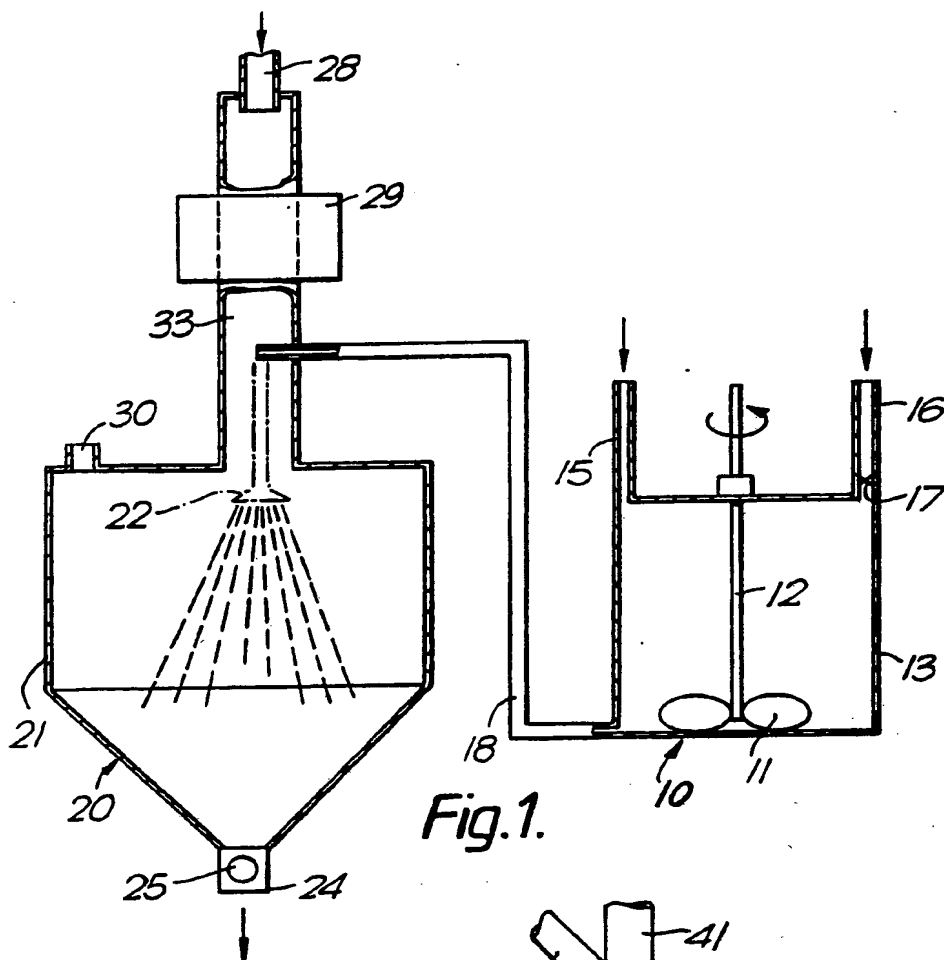


Fig. 1.

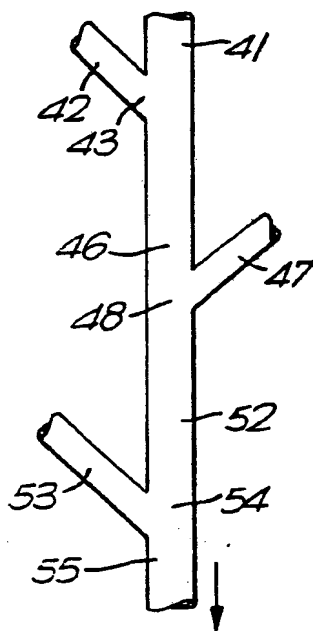


Fig. 2.

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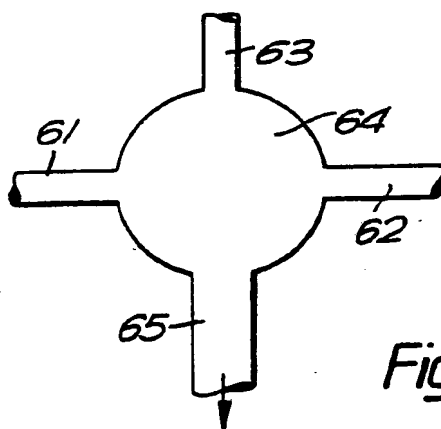


Fig. 3.

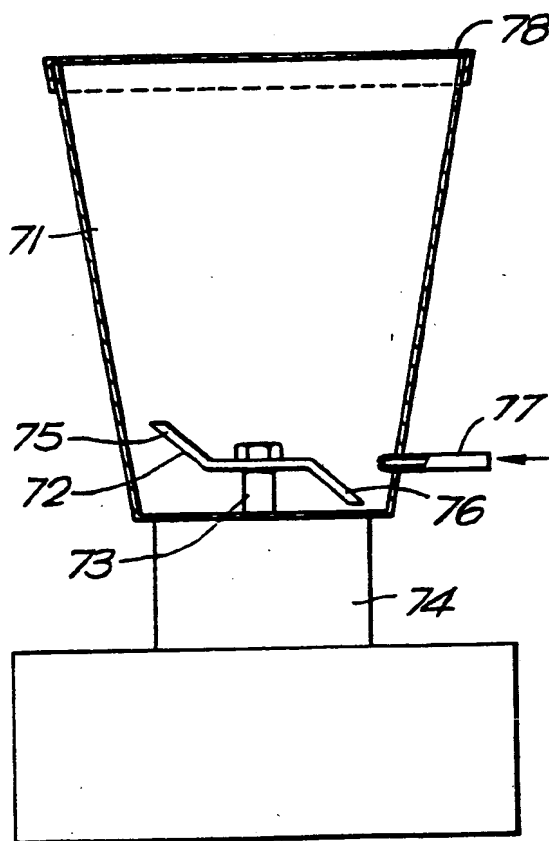


Fig. 4.

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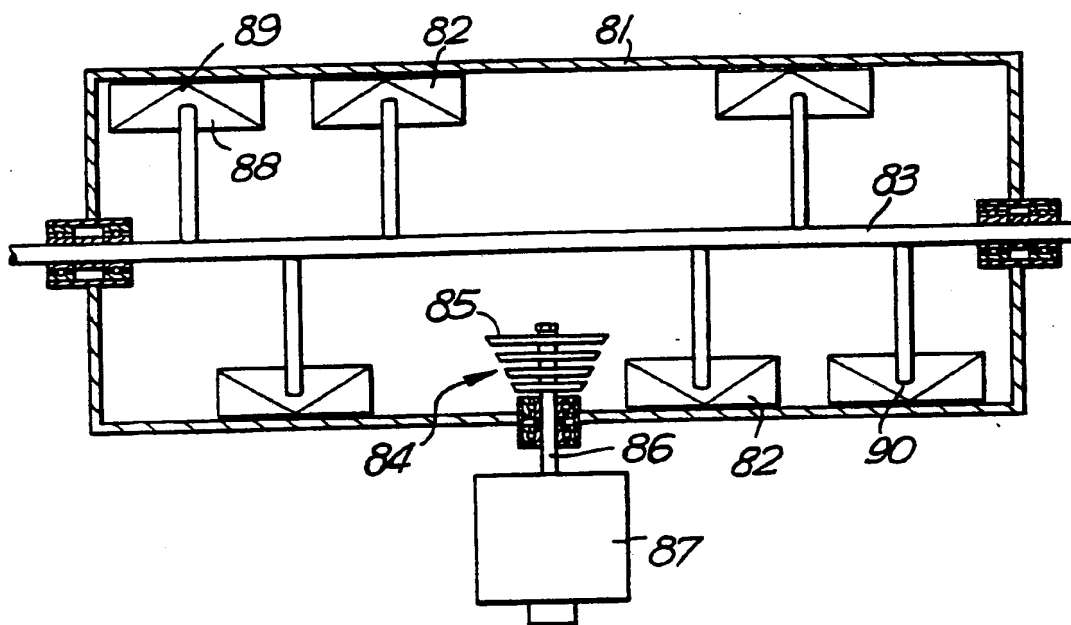


Fig. 5.

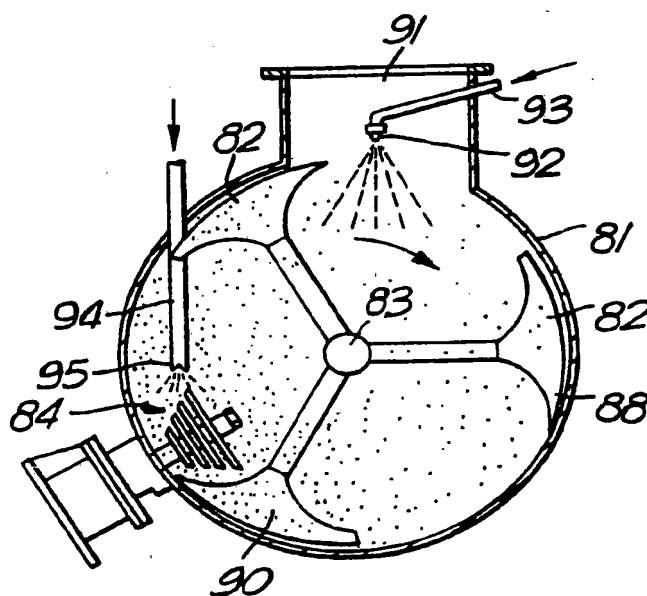


Fig. 6.

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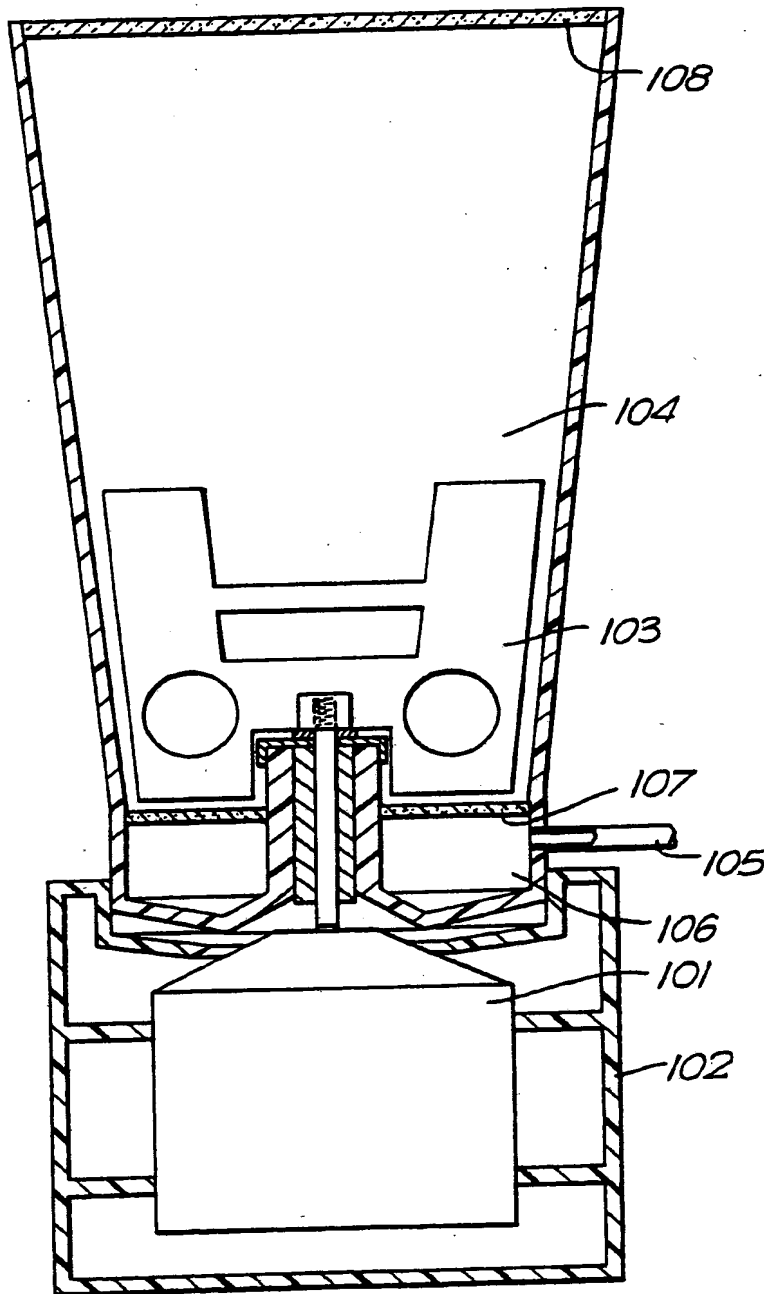


Fig.7.

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*Fig. 8.*

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*Fig. 9A.*



*Fig. 9B.*

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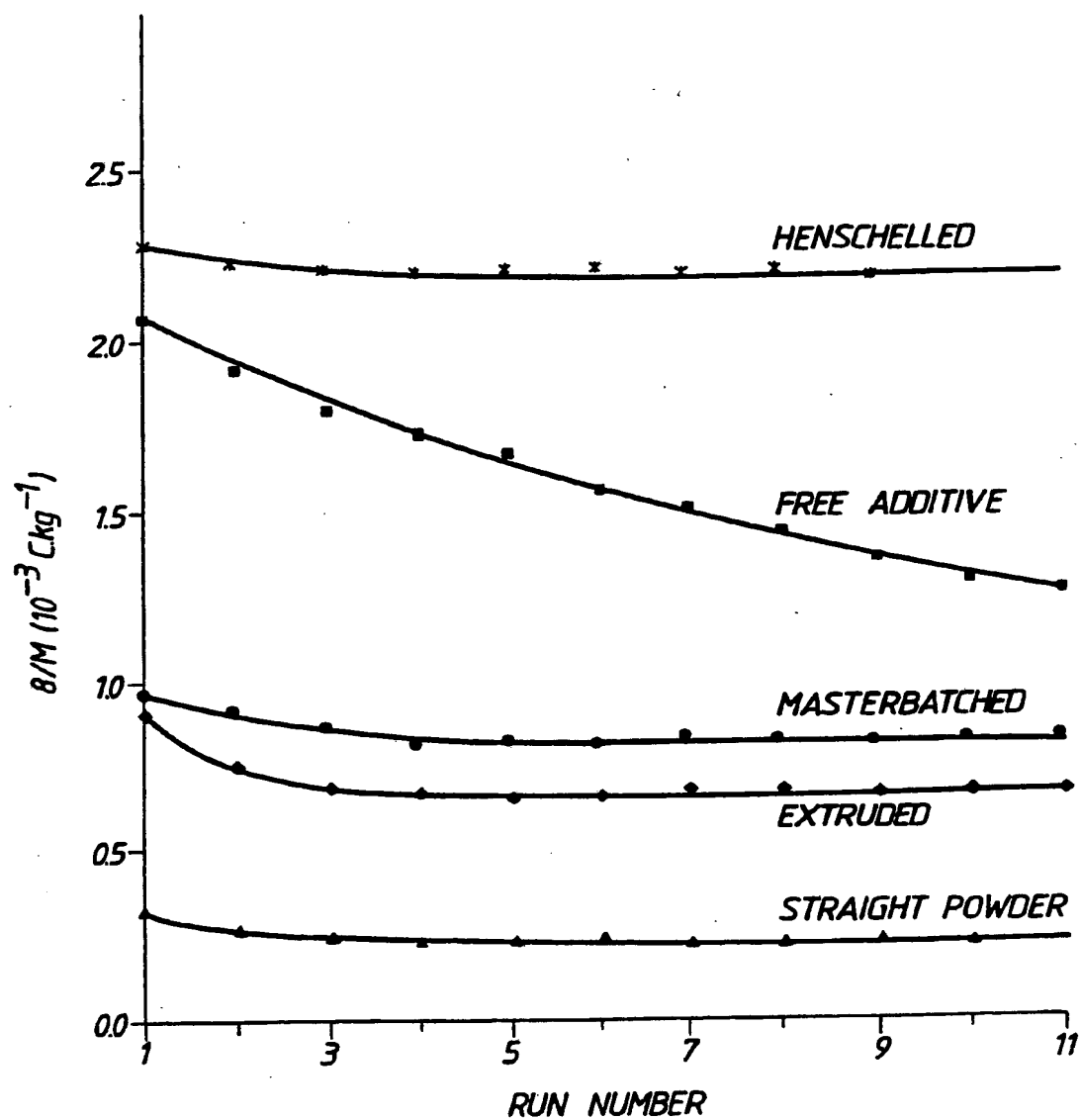


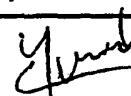
Fig.10.

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 91/00868

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5      C09D5/03 ;      C08J3/20		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C09D ;      C08J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claims No. <sup>13</sup>
P,X	EP,A,372 860 (COURTAULDS COATINGS) June 13, 1990  see claims; figures 1-7 & GB,A,2 226 824 (COURTAULDS COATINGS) July 11, 1990 cited in the application ---	1,6-8, 35-38, 40-43, 46-48
A	US,A,4 260 066 (MARTIN J. HANNON) April 7, 1981 cited in the application see abstract ---	1,4,5
A	EP,A,250 183 (NIPPON PAINT CO.) December 23, 1987 cited in the application see claims ---	1,9
-/-		
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
18. OCTOBER 1991	05. 11. 91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	GIRARD Y.A. 	

III. D DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	DE,A,2 147 653 (STRUMHAUS JAROSLAV) April 5, 1973 see claims ---	1,4,5
A	FR,A,2 310 394 (UNILEVER) December 3, 1976 see claims ---	1
A	US,A,3 980 607 (GERHARD JOHANNES) September 14, 1976 see abstract ---	1,9
A	FR,A,2 190 874 (TOYO BOSEKI K.K.) February 1, 1974 see page 3, line 17 - line 22 see page 7; example 5 see claims 1,2 ---	1,27-29, 45